

Exchange Reactions on Zeolites
and Related Catalysts

by

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SUMMARY

The exchange of hydrocarbons with deuterium makes^a/useful test reaction# for studying catalytic processes and finding out what first happens when the molecules are adsorbed on the catalyst surface. The object of the present study was to examine the catalytic activity of amorphous and crystalline alumino-silicates for these reactions in order to try to elucidate the nature of the adsorbed species and compare the results with those obtained for other classes of catalysts.

The exchange reactions of benzene, toluene, and m-xylene with deuterium have been studied on silica-alumina and alumina catalysts.¹ On these catalysts the hydrogen atoms in the ring positions reacted in preference to those attached to the side groups and there were no appreciable directing effects due to the side groups. The main conclusion drawn is that these catalysts are of an acid nature although there are some differences between the results and those for the homogeneous acid catalysed exchange. Reaction mechanisms are discussed with particular reference to a possible slow step involving surface hydroxyl groups.

The activity of synthetic crystalline alumino-silicates (X-type zeolites) were examined in various ion exchanged forms for hydrogen-deuterium exchange and for the reactions of ethylene, propylene, 1-butene, isobutene, isobutane and m-xylene with D₂O. Most of the zeolites were poor catalysts

for the hydrogen-deuterium exchange reaction but in some cases the activity could be increased by heating in hydrogen. For the exchange of hydrocarbons with D_2O the order of activities of the catalysts were $CeX, LaX > NiX, CoX, CuX > CaX > NaX$. On CeX and CoX the reactivities of the hydrocarbons for exchange were isobutene \gg 1-butene, m-xylene o and p ring hydrogens $>$ propylene $>$ m-xylene m-ring hydrogen $>$ m-xylene side group hydrogens $>$ ethylene, isobutane. Subsidiary experiments were also carried out to determine the variation in catalytic activity with increasing amounts of D_2O and varying degrees of ion exchange.

The results were interpreted in terms of ionic mechanisms which produced heterolytic splitting of hydrogen and hydrocarbon molecules on adsorption. Correlations were found to exist between the reaction parameters for propylene exchange, the charge on the zeolite cations and the trends reported for surface acidities. From thermochemical data it was shown that the ease of exchange of the hydrocarbons paralleled the ease of formation of the corresponding alkyl carbonium ions.

Zeolite catalysts show more resemblance^a to true acid catalysts than was found for reaction on silica-alumina and alumina with the possible exception of NiX which resembles pure metals and may carry out reactions via radical intermediates. The nature of the active site for hydrogen-deuterium exchange and for the reactions of propylene with D_2O are discussed. For

both reactions sites other than the cation seem to be important.

- ¹ McCosh, R., and Kemball, C., J. Chem. Soc. (A), 1555 (1968)

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PART I

GENERAL INTRODUCTION AND EXPERIMENTAL

CHAPTER 1

Introduction to Catalysis

1.1. Historical Background

Although catalytic processes have been carried out since the beginning of civilisation the first scientific observation of a catalytic transformation was not carried out till 1811 when Kirchoff ¹ showed that mineral acids in hot water solution changed starch into dextrose and sugar without being themselves altered by the reaction. Shortly afterwards other catalytic investigations were carried out by Davy ² ^{and} in 1831 Phillips by the use of platinum sponge carried out the air oxidation of SO_2 to SO_3 , a process which half a century later made possible the industrial manufacture of Sulphuric acid by the 'Contact Process'.

The concept of catalysis and catalytic action however, was not introduced into chemistry till 1836 when Berzelius ³ used this classification in order to group together a number of apparently diverse chemical reactions and to indicate that the mechanism of these reactions might be ascribed to a common cause. The first quantitative meaning was given to catalysis by Ostwald ⁴ who at the end of the last century introduced the idea of the velocity of change as a measure of catalytic action. He was probably the first person to satisfactorily define a catalyst when he said "A catalyst is any substance which alters the velocity of a chemical reaction without appearing in the end products". Probably a more acceptable definition is that a Catalyst is a substance which increases the rate at which a chemical system

attains equilibrium. Thus the catalyst must increase the rate of both the forward and reverse reactions without affecting the equilibrium. Since Ostwald's definition of catalysis, progress has proceeded not so much from the assertion of a stricter definition but rather in that the velocity relationships of a very large number of catalytic systems have been obtained thereby giving an insight into their mechanism.

In general catalysed reactions may be divided into two main classes:

- 1) Homogeneous catalysis; where the catalyst and reactants are in the same phase .
- 2) Heterogeneous catalysis; where reaction takes place at an interfacial layer between two discrete phases .

It is with the last these classes that the rest of this thesis is concerned.

1.2. Mechanism of Heterogeneous Catalysis

The first attempt to explain the mechanism of heterogeneous catalysis supposed that the molecules of a gas were brought into a chemically active condition by mere mechanical impact with the surface of the catalyst but this theory was quickly found to be unable to explain many of the aspects of catalysis. Further theories proposed by Faraday ⁵ and Langmuir ⁶ suggested that the catalyst was capable of exerting an attractive force on the reactant molecules thus forming an increased concentration of reactants on the catalyst surface. The resulting increase in

reaction rate may then be explained simply by application of the law of mass action. Although this theory of catalysis is inadequate since it cannot account for the selectivity of certain catalysts for certain reactions, the concept of adsorption developed by Langmuir proves to be very useful in the interpretation of the kinetic data from catalytic experiments. Experimental studies made of adsorption phenomena have established that there are two main ways by which a molecule can be held on a catalyst surface. These types of adsorption are referred to as physical adsorption and chemisorption.

Physical Adsorption

Here the molecules are held on the surface by Van der Waals forces and constitute something like a liquid film. Thus it is to be expected that the forces involved in physical adsorption are similar to those which hold a liquid together. Since these forces are weak they are probably not very important from a catalytic viewpoint except in very special cases ⁷.

However, physical adsorption measurements are useful in catalytic studies since one can obtain values for certain surface properties of the catalyst by measuring the amounts of gas adsorbed under certain conditions. The most important of these is the measurement of surface areas by the method of Brunauer, Emmett and Teller ⁸.

Chemisorption

This type of adsorption consists essentially in the formation

of a chemical compound at the surface of the solid and it involves an exchange or a sharing of electrons between the adsorbate molecule and the adsorbent. The main difference between physical adsorption and chemisorption is manifest in the much larger heat of adsorption of the latter process. Chemisorption, like other chemical reactions, is usually an activated process and so it proceeds at a finite rate which increases with rising temperature. The adsorption is always confined to a single atomic or molecular layer and is highly specific in nature; hydrogen, for example, being chemisorbed by tungsten but not by copper.

The rate of activated chemisorption is often found to obey the Elovich equation:⁹

$$\frac{dx}{dt} = a e^{-b x}$$

where t is time and a and b are constants. The amount adsorbed varies with the pressure of the gas and a simplified treatment by Langmuir ¹⁰ gives the relationship

$$\theta = \frac{ap}{1 + ap}$$

where θ is the fraction of the surface covered by adsorbed molecules, p is the gas pressure and a is a constant related to the heat of adsorption.

Due to the large energy changes which chemisorption brings about in a molecule this process is thought to be a prerequisite of a catalytic reaction and thus the study of heterogeneous catalysis is closely connected with chemisorption studies.

Kinetics and Mechanism

As stated above, a catalytic reaction proceeds through chemisorption of at least one of the reactant molecules. This occurs at specific 'sites' on the catalyst surface and the overall reaction may be divided into five steps:

1. Diffusion of reactant(s) to the catalyst surface from the gas phase.
2. Chemisorption of one or more reactant species on the catalyst surface.
3. Reaction of these adsorbed species either among themselves, with physically adsorbed species, or with other molecules colliding with the surface.
4. Desorption of reaction products from the catalyst surface.
5. Diffusion of products from the surface into the gas phase.

When studying the kinetics of a catalytic reaction it is important to know which of the above steps is the one which controls the rate of the overall reaction. For useful information concerning the mechanism of the surface reaction (3) to be derived from kinetic results it is imperative to ensure that steps (1) and (5) are not rate determining. The simplest method of deciding whether or not a reaction is diffusion controlled is to measure the rate at various temperatures since diffusion processes are not greatly dependent on temperature whereas chemical phenomena usually are. Thus if straight lines are obtained from the Arrhenius plots of widely differing rates this may be taken as

evidence against diffusion being the rate controlling step. More sophisticated methods for determining the effect of diffusion on the overall reaction have been developed by Wheeler ¹¹ but in the present work care was taken to ensure that where possible the reactions were not limited by these processes. The methods for deciding which of the other steps is rate determining are usually based on other kinetic data. One example of this is the work by Kummer and Emmett ¹² who found that the rate of exchange of $^{28}\text{N}_2$ with $^{30}\text{N}_2$ agreed well with the rate of formation of ammonia from nitrogen and hydrogen on a particular catalyst thus demonstrating that chemisorption of nitrogen is likely to be the rate determining step in these reactions.

The exact mechanism of the surface reaction is difficult to determine since the nature, properties and concentrations of the various chemical species cannot easily be derived from the examination of the kinetics of a catalytic reaction. Only techniques such as E.S.R., I.R. and other types of spectroscopy are capable of giving direct information on the nature of surface species and even here the results are often difficult to interpret. Of the indirect methods for finding out about the nature of the chemisorbed species and the surface reaction, experiments using deuterium or other 'tracer' elements have been found to be very useful ¹³. The work in this thesis is mainly concerned with exchange reactions of hydrocarbons with deuterium on zeolite catalysts in an attempt to find out about the nature of the chemisorbed hydrocarbon and its reactivity.

1. 3. Exchange Reactions

Of all tracer studies the use of deuterium has been more widely exploited than any other element. Although deuterium became available for catalytic studies in 1933 progress was limited until the mass spectrometer was adapted as an analytical tool by chemists. The extensive and detailed information about the nature of reactions taking place on catalysts which this instrument provides has resulted in extensive developments during recent years, particularly in the study of exchange reactions of hydrocarbons.

In the early work, the techniques used to follow exchange reactions with deuterium were:

- (a) measurement of the dilution of the deuterium by hydrogen by means of thermal conductivity
- (b) the examination of hydrocarbons by infrared spectroscopy
- (c) the determination of the total deuterium in the hydrocarbon by combustion.

The chief point established by these early investigations was that the exchange of hydrocarbons with deuterium occurs much more readily than the cracking of hydrocarbons despite the fact that C-H bonds are substantially stronger than C-C bonds. With the techniques available at that time it was not possible to discover how the deuterium was distributed among the various positions in the hydrocarbon molecule. This type of information became available only after the mass spectrometric technique of following exchange reactions was introduced.

In recent years the exchange of many hydrocarbons have been studied on various catalysts. In investigations of the exchange of saturated hydrocarbons, apart from a certain amount of cracking which may occur at higher temperatures, one is dealing with a pure exchange reaction and the only effect of the catalyst is the production of different isotopic species with no overall change in the chemical composition of the reactant gases. With unsaturated hydrocarbons other reactions such as deuteration, double bond migration and cis-trans isomerisation may also occur along with exchange ¹⁴ and in these cases techniques such as gas chromatography are useful to supplement the mass spectrometric analyses.

Recent investigations on the exchange of alkyl benzenes have demonstrated the value of this kind of research and the two most important types of information obtained can be summarised briefly as follows:

- (a) data on the catalytic activity of the metal for the breaking and making of different kinds of carbon - hydrogen bonds, based on a classification of the hydrogen atoms in the molecules into groups according to their relative ease of exchange.
- (b) information about the nature of the adsorbed hydrocarbon, derived from a study of the distribution of the isotopic species.

It will be shown in greater detail later that these reactions may also be used as tests for determining the type of reactions

which a particular catalyst will carry out by examination of the activities of the various hydrogen atoms in these molecules.

1.4. Catalysts and Catalytic Activity

General Considerations

The geometrical properties of reactant molecules and the crystal habit of contact catalysts are important considerations in catalytic activity. The earliest and perhaps the most convincing evidence for the importance of steric factors in catalysis has been obtained for hydrogenation reactions and therefore appears to be confined largely to metal catalysts. This information shows that geometrical criteria are important in chemisorption and catalysis in addition to the usual electronic considerations ^{15,16}. Since the work in this thesis is not directly concerned with metal catalysts this aspect will not be discussed further. The relationship between stereochemical considerations and the mechanism of olefin hydrogenation over heterogeneous catalysts has been reviewed in detail by Siegel ¹⁷ and by Bond and Wells ¹⁸.

Another important property to be taken into account when studying catalysts is that of gross physical structure, in particular, specific surface area and pore size distribution. That these properties can be controlled to some extent in the manufacture of solid catalysts does not lessen their importance.

It can be taken as a rather general statement of truth that the activity of unit mass of catalyst increases with its specific

surface area since the activity depends upon the ability of the catalyst to chemisorb at least one reactant and thus would be expected to increase with the surface area. For this reason industrial catalysts like those used in the present work are usually porous solids of specific surface area lying between about 100 and 1,000 m² per gram. With such large surface areas diffusion of reactants to the active surface of a catalyst can often be slower than the intrinsic surface reaction and the resulting mass transport mechanism can thoroughly becloud reaction rate constants, activation energies, phenomenological reaction order and selectivity as deduced from measurements of concentrations in the fluid or gas phase.

As stated previously care was taken whenever possible to avoid these effects so that the measured kinetics were indicative of the surface reaction.

Classification of Catalysts

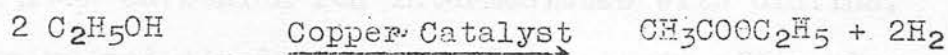
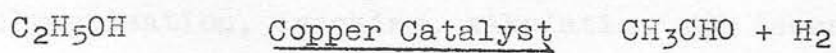
It is possible to divide contact catalysts into categories according to their electrical conductivity and to classify the function of these catalysts as shown in Table 1.1. It is found that most of the catalysts and reactions from the extensive list of Innes²⁰ fit this classification.

The primary catalytic functions of metals are hydrogenation and dehydrogenation; active metals catalyse these reactions by virtue of their ability properly to adsorb reactants and/or products.

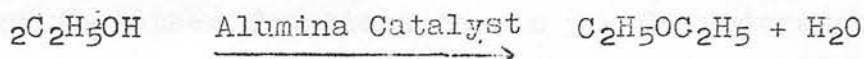
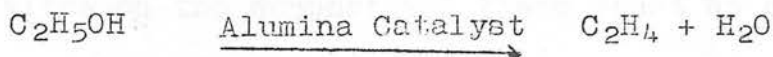
Table 1.1 Classification of Catalysts¹⁹

Catalysts	Metals	Metal oxides and sulphides	Salts and Acid-site catalysts
Electrical Properties	Conductors	Semiconductors	Insulators
Catalysed reactions	Hydrogenation Dehydrogenation Hydrogenolysis (oxidation) (reduction)	oxidation Reduction Dehydrogenation Cyclization (hydrogenation)	Polymerisation Isomerisation Cracking Dehydration Alkylation Hydrogen transfer Halogenation Dehalogenation

Thus the following reactions can be rationalized in terms of copper's ability to weakly adsorb hydrogen:



whereas the same ethyl alcohol undergoes dehydration over alumina in accord with the latter's ability to adsorb water more readily than hydrogen:



The catalytic action of semiconducting metal oxides in oxidation and reduction reactions can be rationalized on a similar basis. Whereas metal oxides of predominantly covalent character are always stoichiometric and are therefore insulators which do not readily adsorb or desorb oxygen, their predominantly ionic cousins exchange oxygen easily. To this latter behaviour are attributed their semiconducting properties as well as their catalytic action in oxidation and reduction reactions. A detailed discussion of the catalytic oxidation of hydrocarbons by metals and non-metals has been given by Margolis ²¹. Care must be taken when attributing oxidation and reduction properties to metal and metal oxide catalysts since under reaction conditions metals may be oxidised and metal oxides reduced.

The polymerisation, cracking, alkylation and isomerisation role of solid salts and acids is believed to be due to their ability to form carbonium ion intermediates with olefins. Thus silica-alumina and alumina supported catalysts often play a dual role and it has been shown by Weisz ²² and others ²³ that platinum supported on silica-alumina is really a dual functional catalyst in reactions like isomerisation and hydrocracking of alkanes. It appears that the alkanes are dehydrogenated on the metal portion of the catalyst and the resulting olefins migrate

to acidic sites on the support and there react by carbonium ion mechanisms.

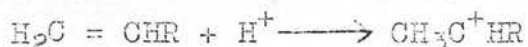
Many of the other functions remain poorly understood even in terms of a general rationale but as the work in this thesis is concerned with catalysts in the insulator category further discussion will be limited to this type.

1.5 Insulators and acid-site catalysts

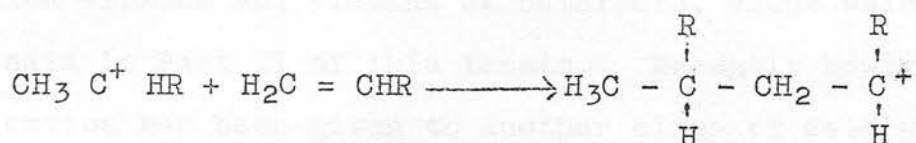
Although these materials comprise a rather small group of catalysts they are very important commercially especially in the Petroleum industry. The best known insulator catalysts are alumina, silica alumina, silica-magnesia, silica gels, phosphates like Al PO_4 and certain clays that have been activated by appropriate chemical treatment. All these catalysts exhibit acidic sites on their surfaces. These sites are often OH groups which can function as proton donors (Brønsted acids); another plausible mechanism of acidic behaviour in some cases is electron pair assimilation by a catalyst site (Lewis acid). These "acid-site" catalysts strongly chemisorb bases and frequently contain a residue of structural water. Their catalytic action is attributed to their acidic properties, and the mechanisms are akin to those of general acid-base catalysis. Tamele ²⁴, and other workers have clearly demonstrated that the cracking activity of silica-alumina catalysts depends strongly on surface acidity. Reactions over acidic catalysts are discussed at length by Olah ²⁵ and Pines ²⁶.

Carbonium-ion intermediates are thought to be involved in isomerisation, alkylation, polymerisation and cracking of hydrocarbons over acid-site catalysts. However, uncertainty remains as to the true nature (Lewis or Brönsted), of the active acid sites with both types found on many catalysts. The structure and identification of acid groups on silica, alumina, and silica-alumina have been discussed in detail by Boehm ²⁷ and the general chemical properties of cracking catalysts by Oblad, Milliken, and Mills ²⁸. In recent studies Sato and co-workers ²⁹ found using silica alumina and alumina-boria catalysts, that protonic acid sites seemed to be responsible for polymerisation of olefins, the cracking of cumene and the disproportionation of toluene to benzene and xylene while non protonic acid sites seemed to be active for the decomposition of isobutane: they also observed that the effectiveness of the protonic sites for polymerisation was insensitive to catalyst composition but the converse appeared to be true for cracking and disproportionation. In another recent paper of interest ^{ch}Swab and Kral ³⁰ suggest that besides the ordinarily necessary acidic cracking sites, basic points on the catalyst surface also play a role in cracking and that this implies that cracking is favoured by "polarity within the surface".

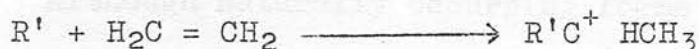
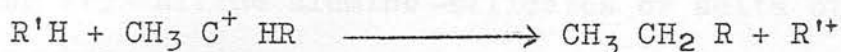
Conceptually the formation of a carbonium ion is most easily represented as proton addition to an olefinic bond:



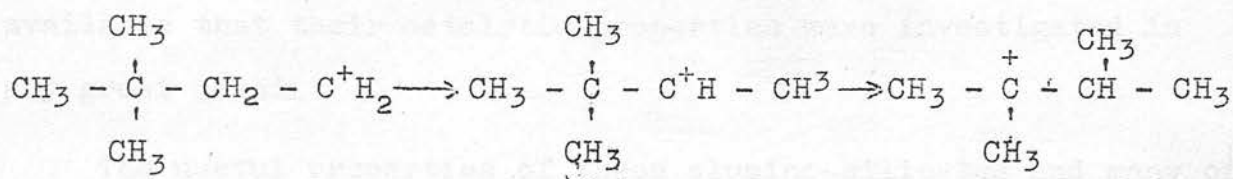
For more complex olefins that ion is formed which has the most alkyl groups attached to the carbonium carbon as discussed by Whitmore ³¹. Subsequent polymerisation can be represented as:



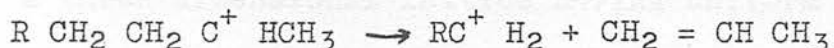
and subsequent alkylation of R'H as:



and isomerisation of a carbonium ion as:



Cracking of carbonium ions occurs by scission at a bond in the β -position to the positive charge:



Thus, given the carbonium ion, all of the above reactions can be rationalised. The unanswered question about these catalysts relate to the exact method of formation of the carbonium ion and how it is bound as a chemisorbed species to the catalyst surface. The exact nature and structure of the active sites on the catalyst surface also remain the object of research.

1.6 Zeolites as Catalysts

The above paragraphs outline roughly the nature and use of silica alumina and alumina as catalysts, about which more will be said in Part II of this thesis. Recently however, much attention has been given to another class of catalysts called molecular sieves or zeolites. These zeolites can be regarded as being crystalline alumino-silicates or salts of alumino silicic acid. Although naturally occurring forms of these minerals were known as early as 1756, when they were discovered and named by the Swedish mineralogist Baron Cronstedt, it was not until 1954 when certain synthetic forms of these minerals became generally available that their catalytic properties were investigated in any great detail.

The useful properties of these alumino-silicates and many of the advantages which they possess over amorphous silica alumina stem from their unique crystal structure characterised by:

- (a) a three dimensional lattice having uniform pores of molecular dimension and possessing remarkable thermal stability.
- (b) a high surface area accessible only to molecules small enough to diffuse through the pores.
- (c) a highly polar surface.

These properties have been found to make zeolites very useful as adsorbents and enable them to effect separations of normal from iso-paraffins and of polar from non-polar molecules.³⁴⁻³⁶ They have found industrial application in the drying of gases resulting

from thermal cracking of petroleum stocks ³⁷, the removal of carbon dioxide and sulphur compounds from natural gas ^{38, 39} and many other processes.

Many of the structural properties of molecular sieve zeolites which are basic to their utility as adsorbents were later found to contribute also to their utility as heterogeneous catalysts. They are already widely used to catalyse cracking and hydrocracking reactions and have also been found useful in catalytic reforming, isomerisation and alkylation processes. In these days of highly developed catalyst technology, a commercial catalyst must have the following performance characteristics to be competitive ⁴⁰.

- (a) Active enough to bring about substantial conversion of the feed at practicable process conditions
- (b) Stable enough to operate for long periods before requiring replacement
- (c) Selective enough to produce a minimum of undesired by-products.
- (d) Strong enough to withstand the normal abuse to which it is subjected during charging and operation of the reactor.

Zeolite catalysts comply with these requirements. Their remarkable thermal stability under process conditions and the mechanical strength of zeolites pelleted with a small amount of clay binder satisfy conditions (b) and (d). They are also very versatile catalysts since by simple pretreatments properties (a) and (c) can be varied to suit many different types of reaction. An excess negative charge on each four co-ordinated alumina tetrahedron in the alumino-silicate crystal framework requires the

inclusion of cations during syntheses. These cations may thereafter be exchanged for other cations or indeed removed if desired. The catalytically active sites are thought to be located at these cation sites and so by changing or removing the cation the catalytic properties of the zeolite can be greatly modified.

The catalytic activity of the alkali metal cation forms of molecular sieve zeolites is primarily radical type, characteristic of materials with high surface areas and low acidity. The alkali metal forms of the zeolites are particularly useful in reactions such as the hydro-dealkylation of toluene to benzene and methane since in this reaction acidic catalysts promote undesired trans alkylation conversions. The multivalent metal ion exchanged and the decationised forms of the zeolites have carbonium ion type activity and are useful catalysts for olefin polymerisation ⁴¹, aromatics alkylation ⁴² ⁴³, alcohol dehydration ⁴⁴ and catalytic cracking processes ⁴⁵. The carbonium ion activity, like that for silica-alumina catalysts has been attributed to the presence of acid sites both of the Brönsted and Lewis acid type. Another explanation is that the strong electrostatic fields within the alumino-silicate crystal lattice are sufficiently energetic to strongly polarize by themselves the C-H bond in hydrocarbon molecule towards the formation of quasi-carbonium ions, thereby facilitating reactions which can occur via a carbonium ion intermediate.

Many catalytically active metals can be introduced into the structure of the zeolite in a cationic form and subsequently

reduced ~~in situ~~ to the elemental state. By this technique extremely high and perhaps atomic dispersion of the metal can be achieved on a high surface area support⁴⁶. These metal .. impregnated catalysts have many uses and sometimes show a behaviour substantially different from their behaviour when they are deposited as agglomerates on a conventional support.

Thus zeolites are very versatile materials for catalytic purposes and since their first introduction in late 1959 they have found widespread use in several major refining and petrochemical applications replacing conventional catalysts like silica-alumina and alumina. Because they are readily tailored to specific applications, the number of applications can be expected to grow as their unusual properties are better understood and appreciated⁴⁷.

1.7 Object of the Present Investigation

In 1964-65 Pope and Kemball⁴⁸ examined the activity of a nickel exchanged X zeolite for the reactions of the alkyl benzenes with deuterium and the purpose of the present investigation was to examine the activity of other ion exchanged forms of zeolites for these reactions.

These catalysts by virtue of their crystal structure contain discrete catalytically active metal ions in a well defined environment. They are thus suitable for basic research work since the surface is well characterised and one can study the catalytic activity of single metal ions in the same environment by using various ion exchanged forms of a particular zeolite. A comparison

of these results with results obtained using metal films and other metal supported catalysts may lead to a better understanding of catalytic processes.

Before investigating these zeolites fully it was felt worthwhile to examine the activity of amorphous silica-alumina for these reactions. Silica-alumina and zeolites, which are crystalline aluminosilicates, are believed to have features in common such as their acidic nature but differ in other respects namely that ion exchange usually destroys the catalytic activity of silica-alumina catalysts while enhancing the activity of zeolites. The behaviour of silica-alumina in many other catalytic reactions has been thoroughly investigated and it was believed that the study of exchange reactions on this catalyst would serve as a basis for comparison with proposed future work on zeolites.

The Catalytic exchange reactions of alkylbenzenes with deuterium were chosen for study. They provide a useful method of investigating catalysts because of the different types of carbon-hydrogen bond present in the alkylbenzenes and the results already reported show striking variations in the relative ability of the various catalysts to bring about the exchange of side-group and ring hydrogen atoms. These reactions have been studied on metal films ⁴⁹⁻⁵¹ supported platinum ⁵² chromium oxide gel, ⁵³ titania ⁵⁴, and nickel exchanged zeolite ⁴⁸. Thus a study of these reactions on silica-aluminas and other zeolites would show to what extent the behaviour of these oxides differed from the other classes of catalysts studied.

Silica-alumina and some zeolites are believed to have acid properties and many of the reactions catalysed by them are similar to those carried out in true acid media. The exchange reactions of the alkylbenzenes have been studied in acid media ⁵⁵ and it was found that there were very large differences in the rates of exchange of the various hydrogens in the benzene, toluene and m-xylene molecules due to the electron donating and directing effects of the methyl side groups. The exchange of these molecules on metal catalysts show a very different behaviour. Thus by examining the activity of silica-alumina and zeolites for the exchange reactions of the alkylbenzenes one can show quantitatively how the activity patterns vary with different classes of catalysts from pure metal films and metal supported catalysts through metal exchanged zeolites and acidic oxides like silica-alumina to homogeneous acid catalysts. These comparisons coupled with detailed examinations of reaction rates and products may help to determine the types of surface intermediates active in catalysis and forecast other types of reactions which a particular catalyst may carry out.

CHAPTER 2

General Aspects of Exchange Reactions

Since there are a number of features which are common to all exchange reactions it is helpful to consider these briefly before describing the method of treatment of experimental results.

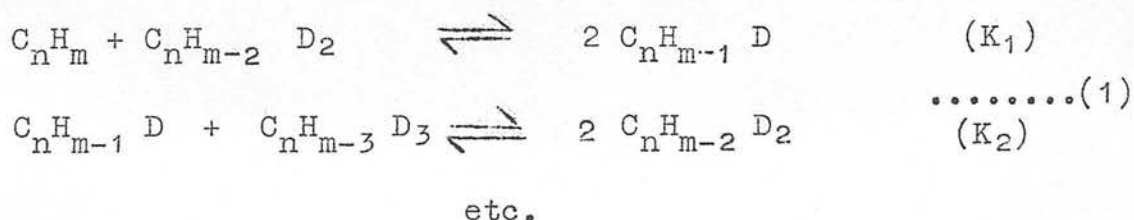
2.1 The Final Equilibrium of an Exchange Reaction

In the exchange reaction between a hydrocarbon C_nH_m and D_2 two kinds of equilibria will be established:

- (a) an equilibrium distribution between the total amount of deuterium in the "hydrocarbon" and the total amount of deuterium in the "hydrogen"
- (b) an equilibrium between the relative amounts of the different isotopic species of hydrocarbons present.

It is found that the distribution of deuterium between the "hydrogen" and the "hydrocarbon" usually differs slightly from the value expected in terms of a random distribution, the amount of deuterium in the hydrocarbon usually being greater than that calculated statistically.

Values obtained for the second type of equilibrium are fairly close to those expected for a random or classical distribution of the hydrogen or deuterium atoms between the various isotopic species of the hydrocarbon. Thus the values of the equilibrium constants for the reactions



can be calculated from a combination of terms in the appropriate binomial expansion and may be expressed in general terms as:

$$K_i = \frac{\binom{i}{m}^2}{(i-1)(i+1)} \dots\dots\dots(2)$$

where the symbol $\binom{i}{m}$ represents the number of ways of selecting i objects from a group of m identical objects. It is found that the interconversion equilibrium constants calculated in this way are in good agreement with experimental results.

2.2 The Determination of Rate Constants

The rate of an exchange reaction may be determined from the parameter ϕ defined by:

$$\phi = \sum i d_i \dots\dots\dots(3)$$

where d_i is the percentage of isotopic species containing i deuterium atoms at time t . If all the hydrogen atoms in the molecule are equally susceptible to exchange and provided that the influence of isotopes on the rate of reaction is ignored, the course of the exchange reaction will be given by the first order equation:

$$\frac{d\phi}{dt} = k_\phi (1 - \phi) = k_\phi (\phi_\infty - \phi) \dots\dots\dots(4)$$

where k_ϕ is a rate constant equivalent to the number of deuterium atoms entering 100 molecules of the hydrocarbon in unit time at the start of the reaction and ϕ_∞ is the equilibrium value of ϕ .

Integrating the above equation we get:

$$\int \frac{d\phi}{\phi_{\infty} - \phi} = \int \frac{k\phi}{\phi_x} dt$$

$$\therefore -\ln(\phi_{\infty} - \phi) = \frac{k\phi}{\phi_x} \times t + C$$

when $t = 0$ $\phi = \phi_0$ (ϕ_0 being the initial value of ϕ)

$$\therefore C = -\ln(\phi_{\infty} - \phi_0) \text{ and } \ln_e x = 2.303 \log_{10} x$$

$$\therefore -\log(\phi_{\infty} - \phi) = \frac{k\phi t}{2.303\phi_x} - \log(\phi_{\infty} - \phi_0) \dots\dots(5)$$

Although equations (4) and (5) are only approximately true because of the assumption that all isotopic species react at the same rate they are found to be obeyed in a great variety of exchange reactions where all the hydrogen atoms in the molecule are equally susceptible to exchange. Failure to obey equation (5) may indicate differences in reactivity between the various types of hydrogen atoms in the hydrocarbon but does not provide unambiguous proof since poisoning of the catalyst may also lead to failure of the equation. For confirmation new equations must be devised but since this is not a feature of all exchange reactions the detailed treatment of these cases will be left until later.

The rate of an exchange reaction may also be calculated from the rate of disappearance of the light hydrocarbon using the empirical first-order equation:

$$-\log(d_0 - d_{\infty}) = \frac{k\phi t}{2.303(100 - d_{\infty})} - \log(100 - d_{\infty}) \dots\dots(6)$$

where d_0 is the percentage of the light hydrocarbon at time t and 100 and $d_{0_{\infty}}$ are the initial and final percentage of this species. If the amount of available deuterium is present in large excess $d_{0_{\infty}}$ will be very small and so equation (6) may be simplified to:

$$-\log d_0 = \frac{k_1 t}{230.3} + 2 \dots\dots\dots(7)$$

The ratio of the two rate constants in equations (5) and (6) defined as:

$$M = \frac{k_1}{k_0} \dots\dots\dots(8)$$

is an important quantity because it represents the mean number of hydrogen atoms replaced by deuterium atoms in each molecule of the hydrocarbon undergoing exchange in the initial stages of the reaction.

2.3 Kinetics

Unlike the rate constants of an ordinary chemical reaction, those described above are constant only for the course of an exchange reaction with a single mixture of reacting gases. They are dependent on pressure and assume different values if the initial pressure of the reactants are altered and so the true kinetics of an exchange reaction can only be determined by carrying out a series of experiments with different mixtures of the reactants, because the course of a reaction with a single mixture follows the apparent first order equation (5).

The reason for the apparent first order behaviour for the

course of an exchange reaction, irrespective of the true kinetics may be seen from a consideration of the processes occurring during the reaction. When the reaction mixture is admitted to the catalyst, two things happen:

- (a) the surface concentrations of adsorbed species build up to their equilibrium values and thereafter remain constant.
- (b) the exchange reaction will commence and will eventually lead to equilibrium between all species in the system, including molecules in the gas phase as well as adsorbed species.

Process (a) will probably be rapid but process (b) cannot go to completion until all the gas phase has been adsorbed and desorbed and throughout most of the time required for the exchange reaction there will be equilibrium concentrations of the different types of adsorbed species. The only factor which reduces the rate of exchange from the initial value is the approach of the isotopic content of the "hydrogen" and the "hydrocarbon" to their equilibrium values and this leads to the apparent first order behaviour.

2.4 Classification of Exchange Reactions and Possible Mechanisms

Exchange reactions of hydrocarbons with deuterium can be separated into two main categories, viz., processes which give stepwise replacement of hydrogen by deuterium and those which lead to multiple exchange. Both processes can occur together although they will be treated separately.

Simple or Stepwise Exchange Reactions

In this class of exchange reaction, only a single hydrogen atom is replaced by a deuterium atom in each molecule which reacts on the surface of the catalyst. Isotopic species containing two or more deuterium atoms are formed only by successive reactions. This class of reaction can be recognised in three ways:

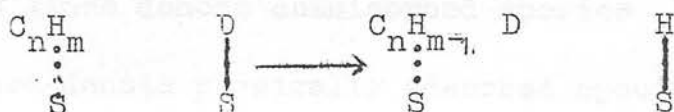
- (a) the value of M defined by equation (8) will be unity.
- (b) the only initial product will be the monodeutero species.
- (c) the interconversion equilibria will be satisfied throughout the course of the reaction, provided that the isotopic species of the hydrocarbon used as reactant are in equilibrium and provided that all hydrogen atoms in the molecule are equally susceptible to exchange.

The first two of these criteria are obvious and the third may be proved quite readily ³².

If an examination of the features of the exchange of a particular hydrocarbon indicates, by the above criteria, that a simple exchange process is operating, the following possible mechanisms must be considered.

- (a) the hydrocarbon molecule is not chemisorbed except during the actual exchange which takes place with a chemisorbed deuterium atom. Thus for C_nH_m , the reaction may be

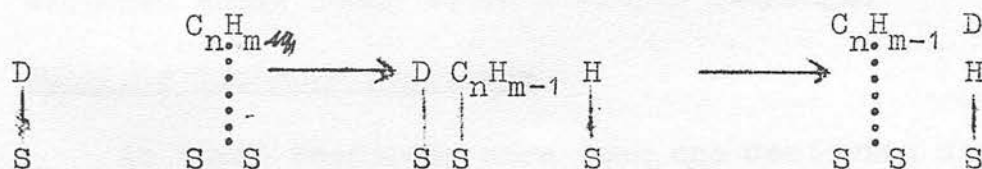
depicted as:



where S represents the surface of the catalyst

- (b) The mechanism may be dissociative and involve adsorbed radicals or ions of the type C_nH_{m-1}
- (c) The mechanism may be associative and involve adsorbed species of the type C_mH_{m+1} which may be radicals or ions.

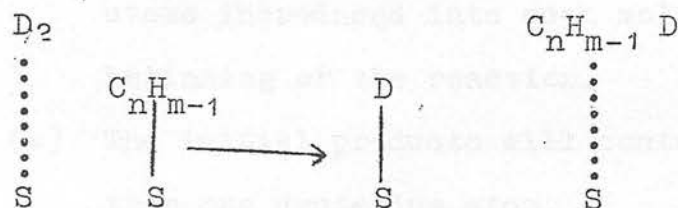
Further data on the kinetics of the reaction, the nature of the adsorption of the reacting gases, and the probable stability of the different kinds of intermediate species are needed to choose between these three possibilities. The evidence suggests that mechanism (b) applies for the exchange of saturated hydrocarbons and mechanism (c) for the exchange of many unsaturated hydrocarbons; there is no evidence that mechanism (a) applies to the exchange of any specific compound, but it is a possibility which must be considered. As with other types of catalytic reactions, it is possible to represent the detailed operation of either the dissociative or associative mechanism in more than one way. Even if it is established that the dissociative process operates it may not be easy to formulate the precise mechanism. It may consist of a Langmuir mechanism where all the species are chemisorbed,* i.e.



* continuous lines denote chemisorbed species

dotted lines denote physically adsorbed species

or alternatively, of an Eley - Rideal mechanism where one of the reacting species is gaseous or physically adsorbed, i.e.,



Detailed arguments have been put forward in support of each of these types of mechanism for the exchange of hydrogen and deuterium,, but there is no clear evidence that one of these mechanisms operates to the total exclusion of the other.

The existence of a simple exchange process implies that the adsorbed intermediate, whether it is of the dissociative type C_nH_{m-1} or the associative type C_nH_{m+1} , must be a comparatively stable entity on the surface of the catalyst. The species must have little chance of undergoing further reaction involving the introduction of a second deuterium atom into the molecule during its lifetime on the surface, because this would give rise to the formation of products with more than one deuterium atom and the exchange would cease to be a simple exchange.

Multiple Exchange Reactions

In these reactions more than one deuterium atom is introduced into the molecule on each interaction with the catalyst surface. The existence of such a process may also be recognised in three ways, exactly analogous to those described above for simple exchange reactions:

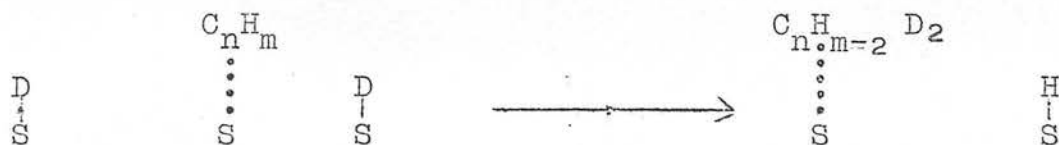
- (a) The value of M defined by equation (8) will be greater than unity and will give the average number of deuterium atoms introduced into each molecule reacting at the beginning of the reaction.
- (b) The initial products will contain species having more than one deuterium atom.
- (c) The distribution of isotopic species during the course of the reaction will be richer in more highly deuterated species than calculated distributions based on equation (2).

Care must be taken however in the use of the above criteria. The distribution of products must be measured at low conversions in order to exclude

1. species formed by successive interactions with the catalyst if criteria (b) is used and
2. the effect of the onset of equilibrium if criteria (c) is used since at equilibrium the distribution of isotopic species will be the same irrespective of whether the exchange is by a simple or multiple exchange process.

The possible mechanisms which can lead to multiple exchange are necessarily more complicated than those involved in simple exchange reactions and four possibilities may be considered.

- (a) No chemisorption of the hydrocarbon except during the actual exchange:



- (b) The formation of a single type of dissociated species involving the loss of at least two hydrogen atoms from the original molecule.
- (c) The formation of a single type of associated species having two hydrogen atoms more than the original molecule.
- (d) The existence of two or more types of adsorbed species of different states of hydrogenation with multiple exchange resulting from the interconversion of these species on the surface of the catalyst.

As chemical changes are usually more rapid the smaller the number of bonds which have to be broken and re-formed during the reaction, mechanism (d) might be expected to be the most common type and mechanism (a) the least probable.

Other aspects of exchange reactions and the results obtained with some hydrocarbons have been reviewed by Kemball ³³.

CHAPTER 3

Apparatus for Studying Exchange Reactions

3.1 Introduction

The work in this thesis is divided into two parts. Most of the results in Part II were obtained during 1965-66 at the Chemistry Department of the Queens University, Belfast. Subsequently work described in Part III was carried out at the University of Edinburgh.

The apparatus used in Belfast was already in existence when the present work was started and the apparatus in Edinburgh was constructed on somewhat similar lines with a few modifications. The apparatus consisted essentially of three parts:

- (a) A high vacuum gas handling system which enabled mixtures of pure gases and liquid vapours of definite composition and pressure to be prepared.
- (b) a reaction vessel coupled to a capillary leak.
- (c) a Mass spectrometer which provided a means of continuous analysis of the composition of the gas mixture in the reaction vessel.

Simultaneous with this research the apparatus in Belfast was used to study reactions on Rutile,⁵⁴ while in Edinburgh exchange reactions on Platinum films were carried out ⁵⁶. These experiments were carried out using the same gas handling systems and mass spectrometers as described in this thesis but using different reaction vessels.

3.2 The Gas Handling System

The design of the gas handling system is shown diagrammatically in Figure 3.1 together with the reaction vessel and evacuation set up. The apparatus was constructed throughout of 'Pyrex' glass and all ground glass taps and joints were lubricated with 'Apiezon L' vacuum grease. Evacuation by means of an Admiralty type diffusion pump and cold trap 'H' backed by a two stage 'Speedivac' rotary pump enabled a vacuum of 10^{-6} mm Hg to be obtained. The vacuum was tested using the McLeod Gauge 'M' (bulb volume 56.3mls).

The apparatus provided facilities for purification of liquids or condensible gases by trap to trap vacuum distillation at 'C'. The purified compounds could be stored either in gas bulbs or in sample tubes attached to the gas line at 'D' and immersed in liquid nitrogen. The latter method of storage was essential for the alkyl benzenes used in Part II of this thesis since prolonged exposure of taps to these vapours caused them to 'streak' due to the hydrocarbon dissolving in the tap grease, and also the purity of other gas mixtures prepared in the gas line was affected by desorption of these vapours from the tap grease.

Crude deuterium was admitted to a storage bulb at 'A' from a lecture bottle equipped with a pressure reducer and needle valve. The deuterium was further purified before use by diffusion through the heated palladium thimble 'J' and then passed through liquid nitrogen traps at 'C'. A similar procedure was used in the purification of hydrogen.

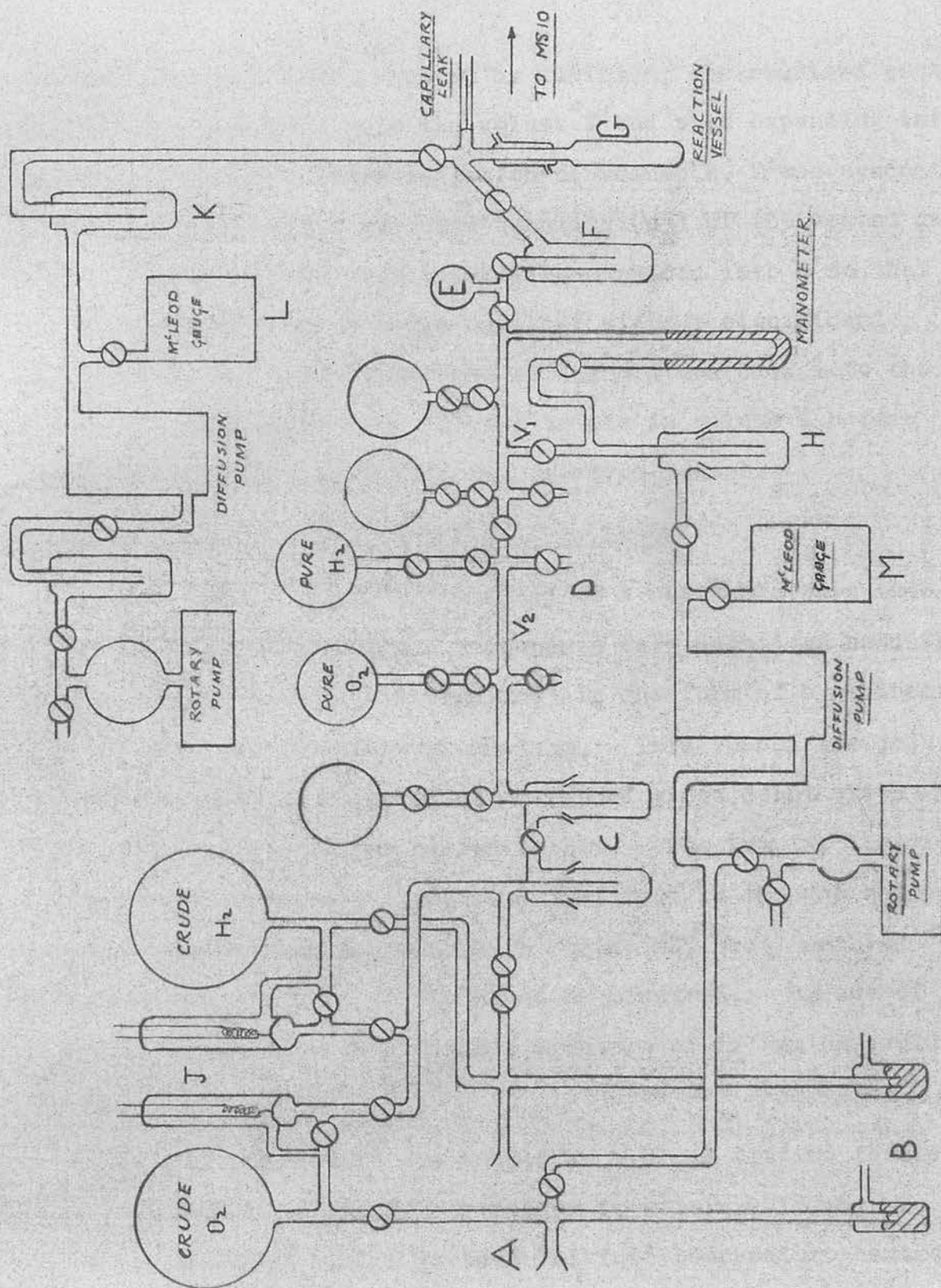


FIGURE 3.1

APPARATUS

Gas mixtures were prepared by admitting the required pressure (p_1) of one component into the volume 'V' and then expanding into the volume 'V' + 'E'. After isolation of volume 'E', 'V' was evacuated and then filled with a measured quantity (p_2) of the second gas ($p_2 > p_1$). Volume 'V' was then quickly re-expanded into 'E' so that the pressure in 'V' and 'E' would equalise without significant diffusion of the first component of the mixture back into the volume 'V'. The gases were allowed to mix in volume 'E' before expansion through a trap 'F' to the reaction vessel.

3.3 The Reaction Vessel and Capillary Leak

The reaction vessel 'G' consisted of a removable part made of silica glass ('pyrex' glass components were sometimes used when high temperatures were not required) in the form of a cylinder 4 cms in diameter and about 1/4 cms long. This vessel was joined to the apparatus by means of a B24 ground glass joint which fitted into a 'pyrex' water cooled socket. The pumping line for the reaction vessel was similar to that used in the gas handling system. The McLeod gauge 'L' (bulb volume 285.5ccs) enabled pressures greater than 10^{-6} mm Hg to be measured. By use of a liquid nitrogen trap at 'K' dynamic pressure of 10^{-6} mm Hg could easily be obtained.

The reaction vessel was heated by a close fitting furnace whose temperature could be controlled to within 0.1°C by use of a variac in series with a Fielden "Bikini" temperature controller. The temperature of the reaction vessel was measured by a T_1T_2

thermocouple connected to a "Sangamo Weston" multi-range millivoltmeter. Since the millivoltmeter imposes a load on the thermocouple circuit which varies with the range setting of the instrument separate temperature calibrations were necessary for each range. These calibrations were carried out using a platinum resistance thermometer, the resistance of which was measured by a bridge circuit and the temperature then calculated using the expression:

$$T^{\circ}\text{C} = 50 + 3348.962 \pm 33.48962 \sqrt{10300.83 - \text{pt} \times 5.972}$$

$$\text{where pt} = 100 \times \frac{R_T - R_0}{R_{100} - R_0} \quad \begin{array}{l} R_0 = \text{resistance at } 0^{\circ}\text{C} \\ R_{100} = \text{resistance at } 100^{\circ}\text{C} \\ R_T = \text{resistance at temp} = T \end{array}$$

Linear relationships between temperature and millivolts were found to apply over each range of the meter. The results are presented below:

Range mV	Resistance Ω	$^{\circ}\text{C}/\text{mv}$
7.5	15	31.8
15	30	28.2
30	60	26.4

Analysis of the gas mixture in the reaction vessel was effected by means of a fine tapering capillary leak attached to the reaction vessel which enabled a small continuous stream of gas to be drawn into an MS10 mass spectrometer. The capillary leak was constructed from 'pyrex' glass by partially collapsing

a piece of 8mm bore tube and drawing it out into a fine capillary. The length of the capillary was adjusted to give a leak rate of about 20mm air into a volume of 20mls in 20 mins with a pressure differential of one atmosphere. The usual length of the capillary was about 15 cms. Such a capillary, similar to that used by Nier,⁵⁷ was found to provide an adequate sample for mass spectral analysis over a period of 12 hours without appreciably depleting the gas in the reaction vessel.

The properties of capillary leaks and the importance of leak design have been discussed by various authors⁵⁸⁻⁶⁰. The conclusions reached were that gas flow through a capillary leak can occur by two processes:

- (a) viscous flow
- (b) molecular flow

If viscous flow predominates, the gas leaking into the mass spectrometer will have the same composition as that in the reaction vessel, whereas if molecular flow is occurring there will be discrimination against the higher mass elements in the gas mixture. Thus a satisfactory leak should permit viscous flow and not molecular flow.

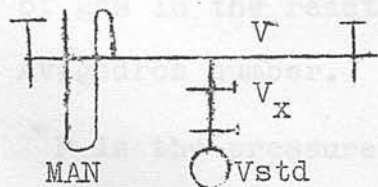
In exchange reactions of hydrocarbons the effect of molecular flow in the capillary leak on the exchange results is usually neglected. It is assumed that the relative amounts of the various isotopic hydrocarbons leaking to the mass spectrometer exactly mirror the composition of the gas in the reaction vessel.

The error in this assumption is usually small since molecular flow is usually only occurring to a minor extent and anyhow the masses of the isotopic species involved are usually so similar as to make the fractionating effect of molecular flow very small. This is not the case, however, when studying hydrogen/deuterium exchange since we are dealing with gases whose masses differ by a factor of two. Thus, any molecular flow in the capillary leak will tend to make the gases flowing into the mass spectrometer richer in hydrogen than the gas in the reaction vessel, and this must be taken into account when analysing the results.

3.4 Volume Calibrations

Volumes of various sections of the apparatus were determined using Boyle's law by expanding air from a measured standard bulb attached at 'D' into the various volumes to be calibrated.

The volume of the standard bulb was found, by calibration with water, to have a volume of 143.3mls at 20°C. The volume of the connecting piece 'V_x' between the standard volume 'Vstd' and the volume



to be measured 'V' was calculated by expanding a known pressure of gas from 'Vstd' into the previously evacuated volume 'V' + 'V_x'

$$\therefore P_1 V_{std} = P_2 (V + V_x)$$

A second expansion was carried out from the volume 'V' into the previously evacuated volumes 'V_x' + 'Vstd'

$$P_3 V = P_4 (V_x + V_{std})$$

knowing the pressures P_1 , P_2 , P_3 and P_4 measured by the manometer and taking into account that the volume V' will vary with pressure in an easily calculable manner, the volumes V' and V'_x can be found. In this case V'_x was found to be 11.0 ml. The other apparent volumes calculated are given below:

Reaction vessel G at	0°C	=	200ml
" " "	23°C	=	190ml
" " "	100°C	=	168ml
" " "	200°C	=	145ml
ice trap F at	0°C	=	97ml
mixing bulb E at	23°C	=	560ml
dosing volume V_1 at	23°C	=	$60.5 + 0.15P^*$ ml;
dosing volume V_2 at	23°C	=	116.5ml

Using these figures the pressures of gases expanded to the reaction vessel at various temperatures can be calculated from a knowledge of the pressures in the dosing volumes. The number of molecules of gas in the reaction vessel can also be calculated using Avogadro's number.

*P is the pressure in the volume V_1

3.5 The Mass Spectrometers

Two mass spectrometers were used in this research. The work in Part II of this thesis was carried out in Belfast using a Metropolitan Vickers MS2 mass spectrometer and the results in

Part III were obtained in Edinburgh using an A.E.I. MS10 mass spectrometer in various modified forms. Since the majority of the research concerned the latter instrument, and since some work was carried out on the development and adaption of this mass spectrometer for studying exchange reactions, discussions will be on this instrument with only a brief description of the other mass spectrometer.

The MS2

This was a general purpose 90° sector instrument suitable for the analysis of gases and volatile liquids. The gases from the reaction vessel passed through a capillary leak, described above, into the ionisation chamber where a tungsten filament was used to produce the ionising electrons. The mass spectrometer was operated using an accelerating potential of 1975 volts and a trap current of 100 μ A. The ionising electron voltage was stabilised at values between 13 and 17 eV in order to reduce the fragmentation of the hydrocarbon. Mass spectra were obtained by varying the magnetic field around the analyser tube and the ion beam intensities falling on the collector plate were amplified and displayed on a 'Sunvic' pen recorder which incorporated an automatic range changing device. This device enabled peaks to be drawn on the highest sensitivity range possible thus ensuring maximum accuracy of measurement. The resolution of the mass spectrometer was about 180.

The MS10

Figure 3.2 shows the arrangement of the A.E.I. MS10 mass

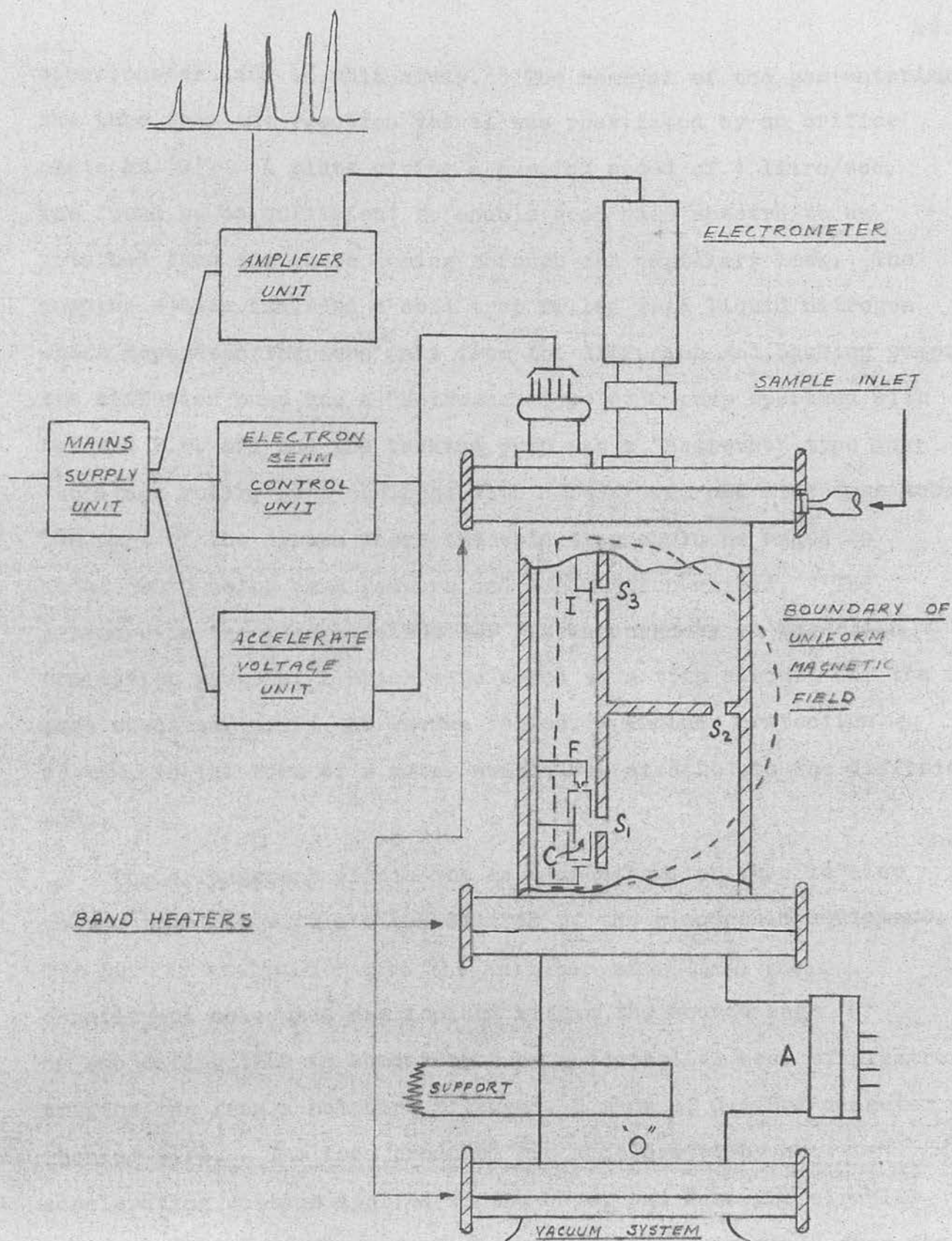


FIGURE 3.2

MS 10 MASS SPECTROMETER

spectrometer used in this study. The removal of the gas entering the tube from the reaction vessel was restricted by an orifice plate at 'O'. A plate giving a pumping speed of 1 litre/sec. was found to be sufficient to enable good mass spectra to be obtained from the gases coming through the capillary leak. The pumping system included a cold trap filled with liquid nitrogen which separated the tube unit from the diffusion and backing pumps. The diffusion pump was a "Metrovac" type 0330 pump operated with Apiezon B.W. oil and the backing pump was a "Metrovac" type GDRI . . two stage rotary pump equipped with a P_2O_5 trap and discharge tube. The part of the system above the cold trap could be baked to about $300^{\circ}C$ using band heaters and a radiation shield. The pressure in the mass spectrometer was measured by an insertion ionisation gauge at 'A' which also acted as a trip circuit for the mass spectrometer if the vacuum failed. Another protection circuit in the form of a water switch was attached to the diffusion pump.

The arrangement within the mass spectrometer tube is also shown, together with a block diagram of the electronic equipment. The gas for analysis enters the analyser tube where the constituent molecules are ionised within the source cage 'C' by subjecting them to bombardment by a controlled beam of electrons originating from a hot wire filament, 'F' made of 0.178mm diameter rhenium wire. The ions produced are accelerated by an accelerating voltage applied to the cage, and describe circular orbits under the influence of the uniform magnetic field from the

magnet. The radius of orbit varies with the ratio of m/e for the ion, (m = mass; e = charge), with accelerating voltage V and the applied magnetic field H , according to the following relationship:

$$R = \sqrt{\frac{m}{e} \times \frac{2V}{H^2}}$$

where R = radius of orbit of ion in the magnetic field.

Thus at constant V and H the ion beam is separated into beams of one particular m/e ratio which has an orbit characteristic of this ratio. By varying either V or H the orbit of the ions will be varied and the individual beams may be brought in turn to focus on the collector 'I' by passing through the slits 'S₁', 'S₂' and 'S₃' called the resolving, defining and collector slits respectively.

The resolution and sensitivity of the instrument was largely determined by the size of the slits S_1 and S_3 . Initially the operation of the mass spectrometer was investigated using resolving and collector slit widths of 0.04" and 0.02" respectively. The magnetic field was supplied by a permanent magnet of approximately 1830 gauss and mass spectra were obtained by varying the accelerating voltage. This unit contained ranges allowing masses 2,3,4, 12 to 45 and 18 to 100 to be focused on the collector, the voltage required to focus any particular mass being approximately $\frac{400}{\text{mass number}}$ (assuming singly charged species). This set up was however unsatisfactory for studying exchange reactions of molecules having a mass greater than 40 since above this the resolution between peaks of adjacent mass was not sufficient to enable one to make more than a qualitative analysis

of the exchange reaction.

To overcome this effect an attempt was made to increase the resolution by reducing the collector slit width to 0.01" and making other modifications to the accelerating voltage unit*. This conversion failed initially to give a significant increase in resolution and on closer investigation several anomalous features of operation were noticed. These effects were only apparent soon after the mass spectrometer was switched on or after the magnet had been placed round the tube unit. Then it was found that after the first few minutes of operation the sensitivity and resolution fell to a fraction of their original value and thereafter remained stable. This decrease in sensitivity and resolution was thought to be due to a charge build up on an insulating layer of 'cracked' diffusion pump oil deposited around the tube unit. Several careful cleaning operations involving washing the source and collector components in hot 'Stergene' solutions and rinsing in boiling distilled water did not greatly improve matters and it was only after the tube unit casing was cleaned as well that an increase in resolution over the basic instrument was obtained without any anomalous features of operation. The mass spectrometer in this form was capable of analysing exchange reactions of C₃ and C₄ hydrocarbons although the resolution fell rapidly at m/e values greater than 80. At this stage of development the mass spectrometer was used to study hydrogen/deuterium exchange reactions on zeolites.

* The components were supplied by A.E.I. as a conversion kit (A.E.I. Technical Information sheet A 210)

The final modification made to the MS10 included a further reduction in collector slit width along with modifications to the source unit as well. The permanent magnet was replaced by an electromagnet whose field strength could be varied up to a maximum of 9 kilogauss enabling a mass range up to $m/e = 400$ to be covered using an ion accelerating potential of 250 volts. This conversion^{*} brought the resolution up to around 400 (10% valley definition) when a 0.001" collector slit was used although sensitivity was low. A 0.005" collector slit was found to give adequate sensitivity for accurate experimental work without decreasing the resolution below an acceptable value and^{MS10} was used in this form for exchange reactions of propylene and subsequent experiments. The mass spectra could be obtained by varying either the magnetic field (at a range of speeds) or the accelerating voltage, but the former method was usually used. Spectra were displayed on an A.E.I. 10 inch potentiometric recorder (type 10S) using a 10 mV range plug.

* A.E.I. Technical Information sheet A508.

CHAPTER 4

Treatment of Experimental Results

4.1 Preliminary Procedure

After the catalyst had been suitably activated and contacted with the reaction mixture the temperature of the reaction vessel was raised until a slow reaction was taking place, indicated by the change in the relative heights of the peaks corresponding to the parent molecule and those at higher masses. At this point the temperature was stabilised and scans of the mass spectrum in the region of the parent molecule were recorded at known time intervals. After sufficient reaction had taken place and enough scans had been taken to enable accurate measurements of the rate of change of the peak heights to be made, the reaction temperature was raised and the process repeated at a new temperature. In some cases the reaction could be investigated at several temperatures before the onset of equilibrium.

The first process carried out when analysing the results of an exchange experiment was to plot the peak heights of the various isotopes against time so that by drawing smooth curves through these points accurate pictures of how the peak heights were changing could be obtained. Since in any scan of the mass spectrum each peak was measured at a slightly different time graphs like those above had to be used in order to obtain a measure of the relative amounts of each particular mass at any one particular time; this became more important as the reaction rate increased. After

these smoothed "raw peak" graphs had been drawn a number of times were selected and the mass spectra at these times taken and subjected to further individual treatment in order to determine the percentage of each isotopic species present at that time.

4.2 Isotope Corrections

Many of the elements as they occur in nature contain small amounts of heavy isotopes. Carbon and hydrogen are found in two isotopic forms, ^{12}C and ^{13}C , and ^1H and ^2H or D, thus the mass spectra of hydrocarbons will contain peaks at mass numbers higher than that of the parent molecule due to the presence of small amounts of these heavier isotopes. In the exchange reactions of hydrocarbons the rates of reaction are measured by the increase in these peaks at higher masses as the hydrogens in the hydrocarbon are replaced by deuterium. To obtain an accurate measure of the amount of exchange it is necessary to take into account the contribution to these peaks from the ^{13}C and D originally present in the hydrocarbon. These amounts can be measured experimentally or calculated theoretically since it is found that the ratios $100^{13}\text{C}/^{12}\text{C}$ and $100\text{D}/\text{H}$ remain constant throughout the range of naturally occurring hydrocarbons. These ratios are found to be 1.081 and 0.016 respectively and thus for any hydrocarbon C_nH_m of nominal mass M the heights of the peaks at mass M+1, M+2, etc., can be calculated relative to the peak height PM at mass M by the use of the above factors.

For C_nH_m

$$100 \frac{P_{M+1}}{P_M} = n (1.081) + m(0.016)$$

$$\text{and } 100 \frac{P_{M+2}}{P_M} = \frac{n}{2} (n-1) (1.081)^2 + \frac{m}{2} (m-1) (0.016)^2$$

The values will vary with the isotopic content of the molecules since one is replacing H by D and thus diminishing the contribution to isotope peaks caused by the presence of naturally occurring D. For any isotopic species $C_nH_{m-x}D_x$ the above values of $\frac{P_{M+1}}{P_M}$ and $\frac{P_{M+2}}{P_M}$ are obtained by substituting $m-x$ for m in these equations. The isotopic contribution due to ^{13}C is not affected by the exchange process.

Thus the first process in determining the true extent of exchange entailed the subtraction of these isotopic contributions from peaks at lower masses. This was done in a systematic manner starting with the lowest masses and working upwards to the higher masses using the corrected peak heights at every mass to calculate the contribution to the higher masses. Corrections to peaks more than two mass units higher were usually very small and were neglected as were the small errors introduced by assuming the isotope correction of fragment ions to be the same as that of the parent ion of the same mass. In fact for all hydrocarbons of low hydrogen content the isotope correction due to the presence of

naturally occurring D could be neglected completely without materially affecting the results.

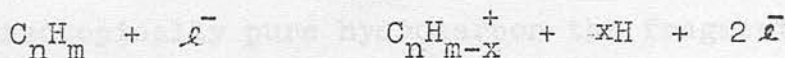
4.3 Fragmentation Corrections

The final corrections made to the peak heights of the mass spectrometer output before true isotopic distributions could be calculated were concerned with the way in which ions are produced in the mass spectrometer.

When the hydrocarbon molecules enter the source region of the mass spectrometer they are subjected to impact from electrons from the filament of the mass spectrometer. When an electron collides with an atom or molecule, energy can be transferred from the electron to the atom or molecule and induce transitions between the energy levels of the system. When the energy of the colliding electron is greater than the ionisation potential of the atom or molecule positive ions can be produced in accordance with the Franck-Condon Principle i.e. for a hydrocarbon C_nH_m we have



However, other processes can occur as well giving smaller positive ions e.g.



Other fragment ions can be obtained through dissociation of C-C bonds but these are usually unimportant in pure exchange reactions. Thus the mass spectrum of a hydrocarbon of mass M will show peaks

at masses M-1, M-2, M-3, etc. due to these fragmentation processes, and so to determine the isotopic content of partially exchanged hydrocarbon molecules the contribution of one isotope to those at lower mass numbers caused by this fragmentation process must be taken into account.

In order to make these corrections as small as possible the mass spectrometer was operated at low electron energies with a small energy spread to make the peak height of the parent ions as large as possible with respect to those for fragment ions. However, as ionisation efficiency (sensitivity) decreased with the electron energy a compromise between sensitivity and fragmentation had to be reached. For most hydrocarbons electron energies between 10 and 20 volts were found to give the best results.

To correct the mass spectrum for these fragmentation contributions the pattern and amount of fragmentation was determined for the neat or isotopically pure hydrocarbon before the exchange reaction took place. This was done before each run as the exact amount of fragmentation varied from day to day. Having calculated the percentage of the fragment peaks with respect to the parent peak of the isotopically pure hydrocarbon the fragmentation for the other isotopic species were calculated statistically.

One can easily see that the fragmentation for each isotopic species is different by comparing the two extremes of the 'neat'

and perdeutero isotopes. The neat isotope, mass M , will have fragments at $M-1$, $M-2$ and $M-3$, etc., but the perdeutero isotope, mass P , which contains only carbon and deuterium can only fragment by loss of two mass units at a time and will only have fragments at $P-2$, $P-4$, $P-6$, etc. In the calculations of fragmentation patterns in this thesis it was assumed that in fragmentation the ease of loss of H and D were the same so that these patterns can be calculated by pure statistics. However, for many hydrocarbons it is found that the molecule tends to loose H rather than D, the ratio of the ease of loss of H to D being about 1.1 and for very accurate analysis this ratio should be determined for the molecule under investigation and the appropriate weighting factors used in the calculation of fragmentation patterns. There is also the complication that at these low electron energies there may not be random loss of H or D in the molecule. The fragmentation of the molecule may occur by preferential loss of H or D at a particular position in the molecule and the pattern will depend on whether this position is occupied by an H or D atom and will be independent of the isotopic content of the other positions. In the present work fragmentation patterns were calculated by pure statistics neglecting any complications arising from the above mentioned processes and it was found that satisfactory results were obtained.

After these fragmentation corrections had been made by a process similar to that used for isotope corrections only starting

at the highest masses, the resultant peak heights which were a measure of the relative amounts of isotopes corresponding to those particular masses were used directly to calculate the isotopic distribution of the hydrocarbon gas entering the mass spectrometer.

4.4 Arrhenius Plots

After isotopic distributions had been calculated at a number of different reaction times at the same temperature, plots of L_{oc} $(\phi_{\infty} - \phi)$ and $L_{oc}/(d_0 - d_{\infty})$ versus time were drawn, according to equations (5) and (6) (Page 24). From the slopes of the resultant lines, which should be straight for an unpoisoned or non accelerating reaction, the initial rates of reaction were obtained and the M value of the reaction calculated.

By use of the Arrhenius equation

$$k = Ae^{-E/RT}$$

$$\text{or } \log_{10} k = \log_{10} A - \frac{E}{2.303 RT}$$

where k = rate constant

A = frequency factor

E = apparent activation energy (cals mole⁻¹)

R = gas constant (cals deg⁻¹ mole⁻¹)

T = temperature in °K

values of E and $\log_{10} A$ were estimated from plots of $\log_{10} k \bar{V}^{1/T^\circ K}$. E was expressed in Kcal/mole and $\log_{10} A$ in mol sec⁻¹ cm².

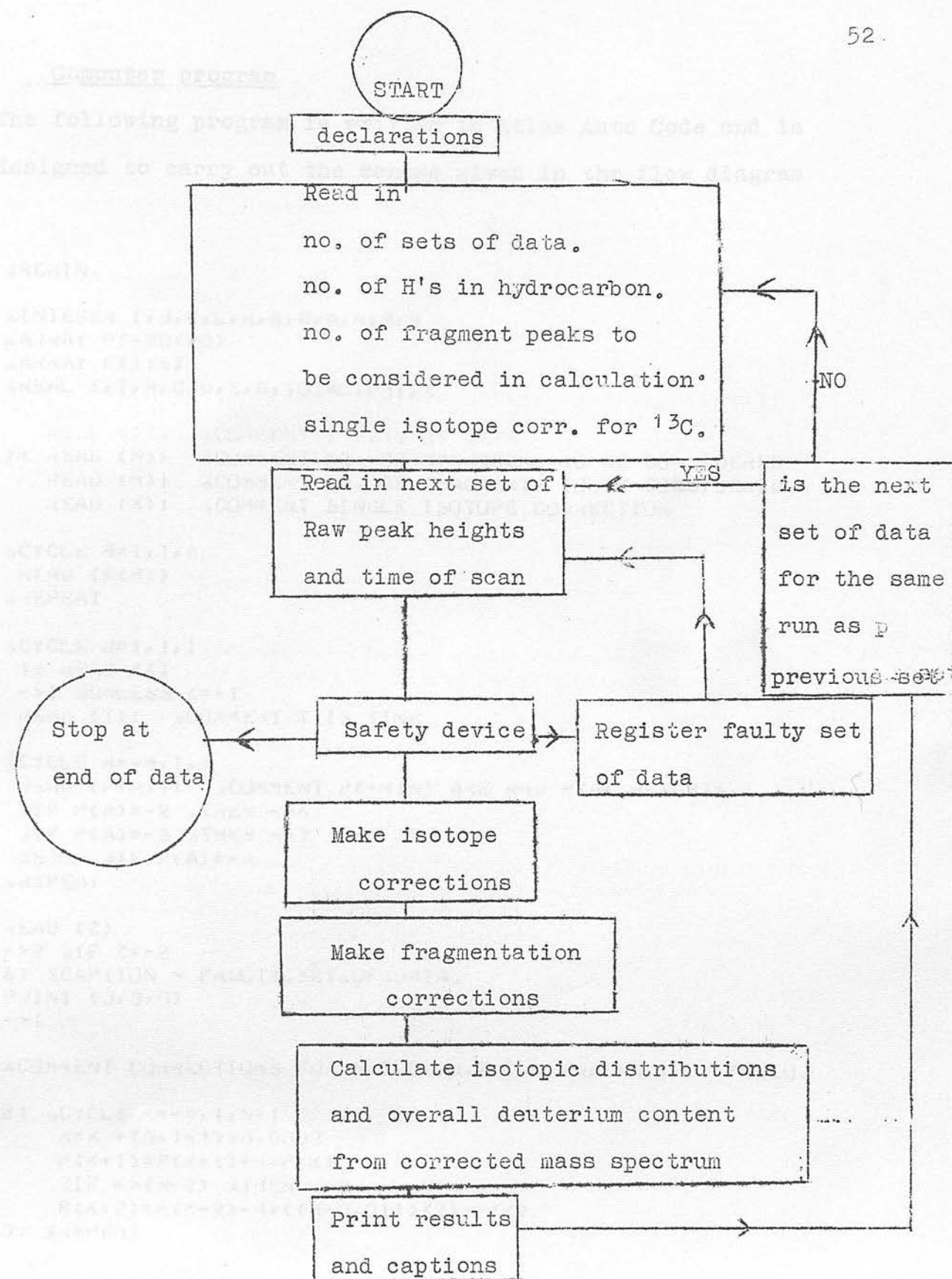
The latter value was calculated from a knowledge of the number of molecules of reactant in the reaction vessel and the surface area

of the catalyst.

4.5 Computer Program for Analysis of Results

Initially the calculation of isotopic distributions from raw peak heights were carried out manually but on arrival at Edinburgh University a computer program was devised to handle the results. Given the fragmentation pattern of the 'neat' hydrocarbon, the isotope correction for ^{13}C , and the number of hydrogen atoms in the molecule this program will calculate isotopic distributions from the raw peak heights. A flow diagram followed by the computer program used is given below.





Computer program

The following program is written in Atlas Auto Code and is designed to carry out the scheme given in the flow diagram

```
%BEGIN
%INTEGER I,J,K,L,R,S,Q,A,N,B,M
%ARRAY P(-20:20)
%ARRAY F(1:6)
%REAL Z,T,H,C,D,E,G,TOTAL,PHI,X

  READ (1) %COMMENT 1 SETS OF DATA
7: READ (N) %COMMENT NO. OF HYDROGENS TO BE CONSIDERED
  READ (M) %COMMENT NO. OF FRAGMENTS TO BE CONSIDERED
  READ (X) %COMMENT SINGLE ISOTOPE CORRECTION

%CYCLE R=1,1,6
  READ (F(R))
%REPEAT

%CYCLE J=1,1,I
  1: READ (Z)
  ->1 %UNLESS Z=-1
  READ (T) %COMMENT T IS TIME

%CYCLE A=-M,1,N
  READ (P(A)) %COMMENT P(-M:N) ARE RAW PEAK HEIGHTS
  %IF P(A)=-2 %THEN ->6
  %IF P(A)=-3 %THEN ->7
  %STOP %IF P(A)=-4
%REPEAT

  READ (Z)
  ->2 %IF Z=-2
6: %CAPTION ~ FAULTY SET OF DATA
  PRINT (J,3,0)
  ->1

%COMMENT CORRECTIONS FOR S.I.C., D.I.C., AND NAT. D. FOLLOW

2: %CYCLE K=-M,1,N-1
  H=X+(N-1-K)*0.0002
  P(K+1)=P(K+1)-H*P(K)
  %IF K>(N-2) %THEN ->3
  P(K+2)=P(K+2)-H*((H-0.011)/2)*P(K)
3: %REPEAT
```

%COMMENT CORR. FOR FRAG. CONS. LOSS OF UP TO 6 MASS UNITS ONLY

%CYCLE L=N₂-1,0

%COMMENT -1

P(L-1)=P(L-1)-(F(1)*((N-L)/N)*P(L))

%COMMENT -2

P(L-2)=P(L-2)-((F(1)*(L/N)*P(L))+(F(2)*((N-L)
((N-1)-L)/(N(N-1))*P(L))) %C

%COMMENT -3

C=P(L)*(F(2)*(2*L/N*(N-L)/(N-1)))
D=P(L)*(F(3)*((N-L)/N*((N-1)-L)/(N-1)*((N-2)-L)/(N-2)))
P(L-3)=P(L-3)-(C+D)

%COMMENT -4

C=P(L)*(F(2)*(L/N*(L-1)/(N-1)))
D=P(L)*(F(3)*3*(L/N*(N-L)/(N-1)*((N-1)-L)/(N-2)))
E=P(L)*(F(4)*((N-L)/N*((N-1)-L)/(N-1)*((N-2)-L)/(N-2)*
((N-3)-L)/(N-3))) %C
P(L-4)=P(L-4)-(C+D+E)

%COMMENT -5

C=P(L)*(F(3)*3*(L/N*(L-1)/(N-1)*(N-L)/(N-2)))
D=P(L)*(F(4)*4*(L/N*(N-L)/(N-1)*((N-1)-L)/(N-2)*
((N-2)-L)/(N-3))) %C
E=P(L)*(F(5)*((N-L)/N*((N-1)-L)/(N-1)*((N-2)-L)/(N-2)*
((N-3)-L)/(N-3)*((N-4)-L)/(N-4))) %C
P(L-5)=P(L-5)-(C+D+E)

%COMMENT -6

C=P(L)*(F(3)*(L/N*(L-1)/(N-1)*(L-2)/(N-2)))
D=P(L)*(F(4)*5*(L/N*(L-1)/(N-1)*(N-L)/(N-2)*((N-1)-L)/(N-3)))
E=P(L)*(F(5)*5*(L/N*(N-L)/(N-1)*((N-1)-L)/(N-2)*
((N-2)-L)/(N-3)*((N-3)-L)/(N-4))) %C
G=P(L)*(F(6)*((N-L)/N*((N-1)-L)/(N-1)*((N-2)-L)/(N-2)
((N-3)-L)/(N-3)((N-4)-L)/(N-4)*((N-5)-L)/(N-5))) %C
P(L-6)=P(L-6)-(C+D+E+G)

%REPEAT

%COMMENT CALCULATION OF PERCENT PHI AND PRINT INSTRUCTIONS

NEWLINES (2)

TOTAL=0

%CYCLE S=0,1,N

%IF P(S)<0 %THEN ->5

TOTAL=TOTAL+P(S)

S: %REPEAT

```
%CAPTION CORRECTED PEAK HEIGHTS
NEWLINES (1)
```

```
%CYCLE R=-M,1,N
  %CAPTION 00: PRINT (R,1,0)
  %CAPTION 01: PRINT (P(R),1,2)
%REPEAT
```

```
%CAPTION ~ TOTAL PEAK HEIGHT, NEGLECTING 0.1 TO 0.05 = 0
PRINT (TOTAL,1,2)
%CAPTION ~ PERCENTAGE OF ISOTOPIC SPECIES
NEWLINES (1)
```

```
%CYCLE R=0,1,N
  %CAPTION 00: PRINT (R,1,0)
  %CAPTION 01: PRINT (P(R)*100/TOTAL,1,2)
%REPEAT
```

```
PHI=0
```

```
%CYCLE Q=1,1,N
  PHI=PHI+Q*P(Q)*100/TOTAL
%REPEAT
```

```
%CAPTION ~ PHI=0: PRINT (PHI,1,2)
%CAPTION ~ TIME=0: PRINT (T,1,2)
```

```
99: %REPEAT
```

```
%END %OF %PROGRAM
```

CHAPTER I

Introduction

1.1 Structure of Silica-Alumina and Alumina

These catalysts are widely used in industry for the hydrogenation of olefins and aromatic compounds. The structure of these catalysts is of great importance in determining their activity and selectivity. The preparation of these catalysts is a relatively simple one, involving the coprecipitation or coagulation of the hydroxides of silica and alumina. Depending on the conditions of preparation, the catalysts can be prepared in a variety of forms, including granular, extruded, and monolith forms.

PART II

EXCHANGE REACTIONS OF BENZENE, TOLUENE, AND *m*-XYLENE WITH DEUTERIUM ON SILICA-ALUMINA AND ALUMINA CATALYSTS.

The purpose of this study is to investigate the exchange reactions of benzene, toluene, and *m*-xylene with deuterium on silica-alumina and alumina catalysts. The results of these experiments are presented in the following chapters. Chapter II describes the experimental procedures used in this study, including the preparation of the catalysts, the deuterium gas, and the reaction conditions. Chapter III presents the results of the exchange reactions of benzene, toluene, and *m*-xylene with deuterium on silica-alumina and alumina catalysts. The results are discussed in terms of the structure of the catalysts and the reaction conditions. Chapter IV presents the conclusions of this study.

CHAPTER I

Introduction

1.1 Structure of Silica-alumina and Alumina

Silica-alumina These catalysts are widely used in industry for the cracking of hydrocarbons and most of the research and investigation into their structure and properties has been carried out using commercially available forms. The preparation of these synthetic silica-alumina catalysts is a relatively simple one, involving the coprecipitation or cogelation of the two hydrous oxides from mixed solutions of sodium silicate and aluminium sulphate. Depending on how the solutions are mixed and on the pH and concentration of the resulting mixture, the combined hydrous oxides will be formed as a coprecipitate, which separates from the greater part of the aqueous phase, or as a true hydrogel which embraces the entire solution volume. This results in the formation of a product having strong zeolitic properties. The sodium ions are then removed by exchanging with another ion such as H^+ , NH_4^+ or AlO^+ , and this is usually done by treatment of the precipitate or hydrogel with a dilute solution of ammonium chloride (or sulphate) or of aluminium sulphate. After the exchange process has been carried out the material is washed free of electrolytes, dried and calcined at temperatures around $700^\circ C$. There are many other methods of preparing active silica-alumina catalysts. These methods include the impregnation of silica gel with an aluminium compound, which is easily converted to the oxide by

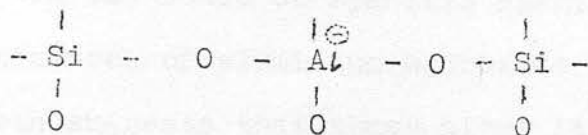
calcination, ^{61,62} and the hydrolysis of mixtures of ethyl orthosilicate and aluminium alkoxides ⁶³. Although only very small amounts of alumina (~0.1%) are necessary to produce an active silica-alumina catalyst more stable catalysts are obtained with larger contents of alumina and so commercial catalysts generally contain around 10% Al_2O_3 and 90% SiO_2 .

There is still some doubt as to the exact nature of the resulting solid prepared by the above methods. It has been suggested that the most probable nature of calcined silica-alumina catalysts is a mixture of silica and alumina particles with the silicon and aluminium ions sharing oxygen ions at the points of contact. If this structure is actually present the chemical properties of alumina in its various crystal forms will be ~~in~~ the main controlling factor of the behaviour of the mixed oxide system. The crystal habits of silica can be expected to be of merely secondary importance in determining the nature of the catalyst. However, recently it has been suggested that silica alumina catalysts, especially the ones containing about 10% alumina are homogeneous throughout and it is only with catalysts of high alumina content or under special pretreatment conditions that the two separate into 'miscelles' of silica and alumina.

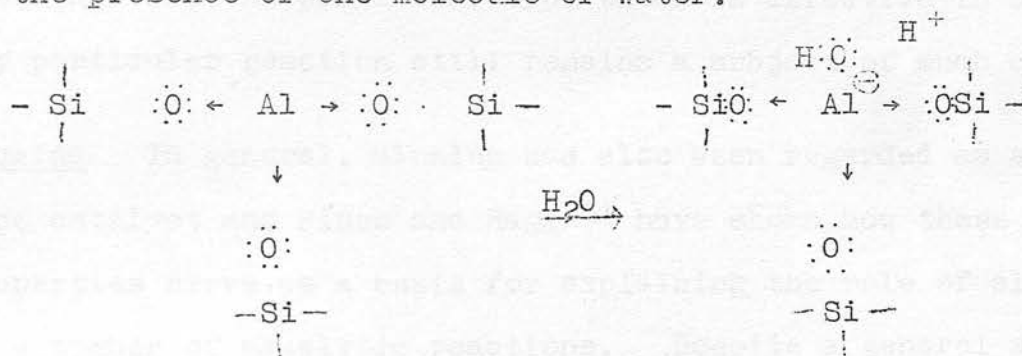
The outstanding chemical property of silica-alumina catalysts is that they display marked acidity. The concept that this acidity was responsible for the catalytic activity was realised on rather indirect evidence. Gayer ⁶⁵ made a significant

contribution to this line of thought when in 1933 he reported that a silica-gel supported alumina catalyst which was active for polymerisation possessed acidic properties. About this time Whitmore ³¹ developed his now classical carbonium ion theory of acid-catalysed organic reactions, including polymerisation and rearrangement reactions of hydrocarbons and in 1940 a review of the then known reactions of hydrocarbons over active aluminosilicates by Frost ⁶⁶ drew attention to the strong similarity of these reactions to those catalysed by acidic substances like aluminium chloride, sulphuric acid and phosphoric acid. It was logical to assume therefore that the activity of silica-alumina was due to an acidic nature.

The bulk structure of silica-alumina has been discussed by Danford ⁶⁷; only the surface structure will be considered here. The acid sites on these catalysts, whose presence and properties will be discussed in detail later, are believed to account for the catalytic activity of silica-alumina due to their ability to form carbonium ions from reactant molecules ⁶⁸. There is still some controversy about the exact nature of the acid sites which bring about certain reactions and many different proposals have been put forward. It is generally believed that acid centres owe their existence to an isomorphous substitution of trivalent aluminium for tetravalent silicon in the silica lattice ^{24, 69}. The resulting structure has been depicted by Hansford ⁷⁰ as follows:

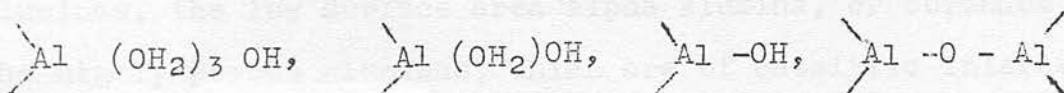


Because the normally six-coordinated aluminium atom has been forced to assume a four co-ordinated structure, there is a net unit negative charge created at this point in the catalyst surface, requiring neutralisation by a cation such as a proton ⁶³. A similar view ²⁴ is that the aluminium atom in such a structure tends to acquire a pair of electrons to fill its p-orbital, creating a Lewis acid in the absence of water and a Brønsted acid in the presence of one molecule of water:



(arrows indicate displacement of electrons towards the Si-O group)

Danforth ⁶⁷ has represented the active site on silica alumina cracking catalysts at various degrees of hydration by the following structures:



Because the most dehydrated form is presumably buried within the bulk structure of the catalyst due to its method of formation, catalytic activity was associated primarily with the Lewis acid

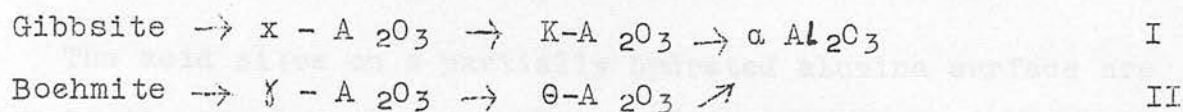
site $\text{Al}-\text{OH}$. On the basis of specific chemical compounds obtained from mixtures of aluminium hydroxide and various methyl silanols Danforth suggests that these sites lie on a chain separated by about 5\AA and explains the exchange with the catalyst of isotopic oxygen from H_2O^{18} and the exchange of D_2O with hydrocarbons by the movement of H_2O , acting as a cocatalyst, along the chains of active sites.

Various other types of site have been postulated but the consensus of opinion is that the most important ones are of the Brønsted or Lewis acid types although the change of one form to the other and the particular type which is effective in catalysing any particular reaction still remains a subject of much controversy.

Alumina In general, alumina has also been regarded as an acid-type catalyst and Pines and Hagg ⁷¹ have shown how these acid properties serve as a basis for explaining the role of alumina in a number of catalytic reactions. Despite a general agreement as to the acidic nature of alumina surfaces an exact chemical description of this acidity has not however been achieved, although some advances along this line have been made by Peri ⁷².

It is well known ⁷³ that there are two general classes of aluminas, the low surface area "alpha" alumina, or corundum, and the highly porous aluminas, which are of catalytic interest. These latter exist in several forms. Thermal decomposition of bayerite gives "eta" alumina, and "gamma" alumina results from the decomposition of boehmite. The dehydration of gibbsite leads to

the formation of various forms of alumina as shown below ^{74,75}.

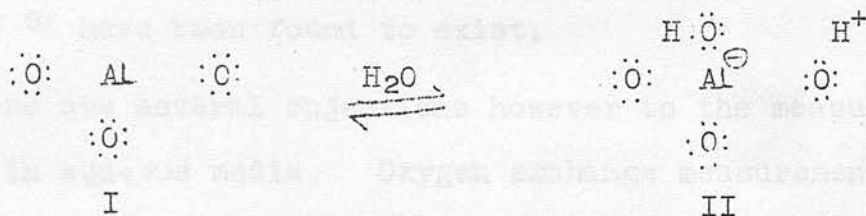


The decomposition proceeds via path I when the gibbsite crystals are smaller than ca. 1μ ; and the coarser crystals produce "transition aluminas" by path II. The various crystal forms of alumina result from the arrangements of aluminium which include either one or both of the possible coordination states, (four fold or six fold), and the ability of alumina ions in crystalline solids to shift from one state to the other is attributed to their ionic size (radius 0.5\AA). The δ alumina structure is a metastable form and changes with temperature. It is formed from boehmite by dehydration at temperatures above about 350°C . On heating to higher temperatures δ alumina loses hydroxyl ions (as water) and gradually shifts to α alumina at about 1000°C . "Chi" alumina changes to "kappa" and α alumina, at about 800°C and 1200°C respectively by a somewhat similar process.

Both "gamma" and "eta" alumina have been regarded as having tetragonally deformed spinel lattices but are structurally dissimilar in that the tetragonal character of "eta" alumina is considered to be much weaker than that of "gamma" alumina ⁷⁶. It has also been shown that the surface areas and pore sizes of these two aluminas differ greatly and since the catalytic properties may be influenced by these surface properties ⁷⁷ it is obviously

necessary to regard structure as an important variable in controlling their catalytic chemistry.

The acid sites on a partially hydrated alumina surface are thought to comprise of both Brønsted and Lewis sites ²¹ although as water is removed from the surface the Brønsted sites are probably changed into Lewis sites. These sites arise from the existence of incompletely co-ordinated aluminium atoms at the surface. When an aluminium atom has an unoccupied p orbital such that it can accept an electron pair it forms a Lewis acid site (I). The presence of a water molecule at this site converts it into a Brønsted acid site (II)



The presence of incompletely co-ordinated surface aluminium atoms can be considered to occur as a result of the defective spinel structure of alumina ⁷⁶. As stated above this structure contains aluminium in four or six fold coordination but at the surface of a dehydrated alumina aluminium atoms with a co-ordination number of three will be present. Vacant cation positions have also been associated with catalytically active sites ⁷⁸.

1.2 Measurement of Acidic Properties

The acidic nature of cracking catalysts can be demonstrated

by their ability to interact with basic substances. Estimations of this acidity have been made by Thomas ⁷⁹ and Grenall ⁸⁰ by titrating the solid in aqueous media with an alkaline base such as potassium hydroxide solution. Other aqueous methods include the liberation of acid from catalysts by means of ion exchange, the measurement of the amount of carbon dioxide liberated from a bicarbonate solution and studies of the rate of inversion of sucrose. Ion exchange using ammonium acetate has also been used to measure acidity. Here one can gain an index of the acidity from measurements of the equilibrium constant between H^+ and NH_4^+ and using this method correlations between acidity and cracking activity ⁸¹ have been found to exist.

There are several objections however to the measurements of acidity in aqueous media. Oxygen exchange measurements ⁸² have shown that water can react with the catalyst surface and thus may alter its properties. Milliken and co-workers ⁸³ argued that the property being measured in aqueous titrations was not acidity but the ability to react with a base, which could be created at the conditions of the experiment. Since under reaction conditions silica-alumina and alumina are in a dehydrated state it is important that acidity measurements be made under these conditions. As the catalysts are activated by outgassing at high temperatures they lose adsorbed water and also some water of constitution. The amount of water left on the surface, usually in the form of OH groups, has been shown to profoundly affect their

ability to catalyse certain reactions. The difficulties arising from the possible interaction of water can be avoided by using non aqueous methods of carrying out acidity determinations such as by adsorption of nitrogen bases either from the gas phase or from non aqueous solvents. Adsorption of the vapours of ammonia or quinoline are advantageous in that studies can be carried out at reasonably high temperatures without any decomposition and using quinoline Ohladi et al⁸⁴ demonstrated that chemisorption took place on calcined silica-alumina at 316°C but not on calcined silica-gel⁷ which is a poor catalyst. Many measurements have been made of the adsorption of these bases and it has been shown that the catalyst activity can be poisoned by the adsorption of as little as 0.2 of a monolayer of these bases. Mapes and Eischens⁸⁵ used infra-red adsorption spectroscopy to study the nature of ammonia adsorbed on silica-alumina. Their results indicated that both Lewis and Bronsted sites were present on this catalyst the former type being more predominant. Tamele² developed a non-aqueous titration technique for acidity measurements. Here the catalyst was suspended in dry benzene and titrated with a benzene solution of n-butylamine using p-dimethylaminoazobenzene as indicator. By studying catalysts of varying alumina content it was found that acidity as measured by titration increased with alumina content to a maximum at 10% and afterwards decreased with further increase in alumina content. The measurement of acid strength of catalyst surfaces by means of dyes has also been used by many workers.

Johnson ⁸⁶ has shown, by this method of Tamele that very few of the aluminium ions in silica-alumina furnish sites of high acidity and Weil-Malherbe and Weiss ⁸⁷ used dyes to show the high acid strength of uncalcined clays. A quantitative interpretation of the significance of these colour changes of dyes was proposed by Walling ⁸⁸. Defining the acid strength of a solid as the ability of the catalyst surface to convert an adsorbed neutral base to its conjugate acid he proposed the H_0 acidity function of Hammett and Deyrup ⁸⁹ as a useful measure of the acid strength of a surface. By these methods Benesi ^{90,91} showed that after calcination at 500-550°C silica-alumina catalysts contained acid sites of the order of $0.6 \mu\text{moles}/\text{M}^2$, and that a small number of these sites had a strength higher than that in 90% sulphuric acid.

Although several aspects of catalytic activity and selectivity can be correlated with acidity measurements using Hammett indicators, the use of these indicators have certain limitations ⁹². Both silica-alumina and alumina ~~possess~~ high Hammett acidities but ~~these~~ acidities of the two substances are different in other respects. It was suggested that at least some of the acidity in silica-alumina was protonic while alumina contained chiefly Lewis acidity. Hammett indicators thus measure the total acidity and not Brönsted acidity alone as has been suggested by Benesi. Hirschler ⁹³ has used arylmethanols and 1,1-diphenylethylene as indicators and concluded from his results that these indicators were specific for measuring protonic acidity. These indicators

distinguished between the acidities of silica-alumina and alumina and alumina and the acidity function H_r derived for these indicators gave much better correlations with catalyst activity than the H_0 functions of Hammett indicators.

Other techniques have been developed to measure acidic properties. Trambouze et al ⁹⁴ developed a method involving thermometric titration of the catalyst in dry benzene with a benzene solution of a weak base like dioxan. They claimed that this method measured Lewis acidity. By using base exchange acidity measurements in conjunction with this thermometric titration they found that with increasing outgassing temperature between 300 and 750°C the number of protonic acid sites, measured by base exchange, of silica alumina catalyst decreased while the Lewis acidity increased, the total acidity remaining constant. Ultra violet and electron spin resonance spectroscopy have also been used in an attempt to obtain measures of the numbers and types of acid sites on catalytic surfaces. Leftin and Hall ⁹⁵ studied the adsorption of triphenylmethane on silica-alumina and were of the opinion that carbonium ions were responsible for the U.V. adsorption band at 420 m μ formed by ~~hydride~~ **hydride** ion abstraction by Lewis acid sites. Rooney and Pink ⁹⁶ have shown that polynuclear aromatics such as perylene form radical ions when adsorbed on dry silica-alumina. By measurements of the electron spin adsorption spectra the numbers of these ions and hence a measure of the number of acid sites involved could be obtained.

While all these methods were clearly decisive in demonstrating the acidity of calcined catalysts the problem of deciding whether the acidity was of the Brönsted or Lewis type was more difficult to resolve. Milliken et al ⁸³ have disagreed with the concept that protons are present on the catalyst under cracking conditions and that they are responsible for the catalytic activity. They agreed that the undried co-precipitate of silica and alumina probably has the structure of a Brönsted acid but they take quite a different view of the chemistry of the calcined catalyst. Their argument is that calcination essentially destroys the Brönsted acid by loss of water from the surface. They also cite evidence to support the belief that agglomeration into a mixture of γ -alumina and silica particles occurs and that the only acidity present is at the aluminium ions at the interface of the γ -alumina and silica miscelles. Another explanation of acidity was also advanced. They suggested that the aluminium ions are mainly in a six co-ordinated state in the structure of silica-alumina and those ions closest to tetrahedral silica are in a state of strain and can be induced to assume tetrahedral co-ordination by the approach of basic molecules. In other words only potential Lewis acid sites were present and these were created at the moment of approach of the base. Hansford however, finds this concept unacceptable ⁷⁰. He argues that only the most polar molecules such as water could exert such an effect on the structure of a solid similar to that which was postulated. The studies on hydrogen exchange between

isobutane and catalysts deuterated with heavy water lend strong support to the belief that protons do exist on the surface of cracking catalysts and are required to activate paraffins for adsorption.

Hirschler ⁹⁷ has disagreed with the suggestion of Leftin and Hall ⁹⁵ that the formation of a triphenyl carbonium ion from triphenyl methane on silica alumina constitutes any proof for the existence of Lewis acid sites on the catalyst surface. He presents evidence to show that triphenyl methane is oxidised to triphenylcarbinol by chemisorbed oxygen and then the trityl ion is formed by reaction with a Brönsted acid site. Hirschler also casts doubt on the use of ammonia chemisorption data for estimations of acid strength distributions ⁹⁸. He shows that desorption of ammonia from silica-alumina at elevated temperatures is accompanied by the loss of a considerable amount of bound water, which may alter and modify the number and strength of the catalyst acid sites.

It has been suggested by Sato et al ²⁹ that calcined silica-alumina catalysts contain both Brönsted and Lewis acid sites and the activity of these catalysts for certain reactions of hydrocarbons can be related to this acidity. Some reactions seem to be favoured by protonic acid sites and others by Lewis acid sites. However, as yet for a number of reactions there is still much controversy about the acid site responsible.

The catalytic activity of alumina has been associated with

the presence of Lewis acid sites and there is general agreement that in the dried catalyst there is little protonic acidity. Peri has been for some time an active researcher in this field. His results have shown that even after drying at 1000°C alumina continues to evolve water on further heating but that above 400°C all the water present is in the form of OH groups ¹⁰⁰. On the basis of infra-red results ⁹⁹ he suggested that in butene isomerisation on alumina these residual OH groups were not directly involved in the isomerisation process and the active sites for isomerisation were of a Lewis acid nature. These conclusions have not been completely accepted however, ¹⁰⁴. The OH groups on a calcined alumina may enter into some reactions. It has been shown ¹⁰⁵⁻¹⁰⁷ that these groups are capable of exchange with deuterium gas at temperatures of 50 to 100°C and thus are not completely unreactive. The OH groups are capable of exchange with ethylene ¹⁰⁸ and may thus enter into reactions such as ethylene hydrogenation ¹⁰⁹. Pines and Haag ⁷¹ report that the acid sites on the alumina surface which are capable of catalysing reactions via carbonium ion intermediates have a range of strengths. The weak sites can cause alcohol dehydration and amine chemisorption but only the strongest acid sites are capable of isomerising cyclohexene. However, when dealing with alumina attention must be paid to the detailed structure. As mentioned before, alumina can exist in several forms and it has been shown that the catalytic activities and acidities of these forms are different ¹¹⁰.

1.3 Reactions of Hydrocarbons on Silica-alumina and Alumina

The main groups of hydrocarbons found naturally include paraffins, olefins, cyclic olefins or paraffins and alkyl aromatics. Much of the work which has been carried out on silica-alumina has been with one or other of these types, the object being to establish broad patterns of behaviour for each group with respect to reactivity. From the bulk of the information compiled, many reactions have been distinguished as being of general significance and these include, among others, cracking, dehydrogenation, polymerisation, hydrogen transfer, isomerisation and coke formation. In the literature more attention has been paid to silica-alumina containing about 10% alumina than alumina itself for catalysing reactions of hydrocarbons. For some reactions alumina is more active than silica-alumina and in others the converse applies, the differences in activity usually being attributed to the differences in acidity. However, for most reactions of importance silica alumina catalysts are usually employed since they are less susceptible to poisoning. The main use for alumina is a catalyst support where in conjunction with metal dispersions it may act as a dual function catalyst and, as such it is widely used in catalytic reforming processes. In the following discussion a brief outline of the significant characteristics of the above mentioned reactions will be given and it will be shown how the carbonium ion theory can be applied in understanding the wealth of known facts.

Cracking, Alkylation and Disproportionation Reactions

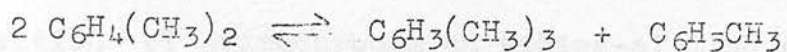
Catalytic cracking is characterised by the extreme complexity of the products obtained from the great majority of individual compounds studied. These products can range in size from methane to coke-like deposits on the catalytic surface and thus it has been very difficult to obtain a clear understanding of primary and secondary reactions. The first important paper on the catalytic cracking of pure hydrocarbons appeared in 1939. In this paper Egloff et al.¹¹¹ reported results on the cracking of several paraffins and olefins in the temperature range 385 to 600°C. They found that the catalytic cracking of n-octane was seven to eight times as rapid as thermal cracking and the product distribution was decidedly different. Paraffins were much more stable than the corresponding olefins in contrast to thermal cracking where they have comparable stability. Greensfelder and Voge¹¹² showed that on a synthetic silica-zirconia-alumina catalyst, carbon-carbon bond rupture is not random as in thermal reactions, but that bonds towards the centre of the molecule are more easily broken yielding fragments of three or more carbon atoms. In the cracking of C₃ to C₂₄ paraffins secondary reactions included isomerisation and saturation of olefins but no direct isomerisation of paraffins was observed. Small quantities of aromatics were also found among the products. It was later found¹¹³ that the presence of tertiary carbon groups enhance the activity of a molecule while quaternary atoms lend stability. Olefins react very readily on cracking catalysts and a wide range of olefinic

materials including aliphatic olefins, diolefins, cyclic olefins and aromatic olefins have been studied ^{111,114}. The reaction product distribution from these olefins yielded a great deal of information on many of the reactions which can occur including polymerisation, isomerisation, hydrogenation and the formation of aromatics and coke residues.

Aromatic compounds have also been studied as these are important components of naturally occurring oils. Thomas et al¹¹⁵ investigated the removal of ethyl, isopropyl, butyl and amyl side chains from the benzene nucleus on silica-alumina and silica-zirconia-alumina catalysts between 400°C and 500°C. In contrast to the cracking behaviour of other types of hydrocarbons, the splitting of side chains higher than methyl from alkylaromatics is a rather specific and clean cut reaction. The side chain is split off at the aromatic ring forming benzene and the corresponding olefin which then undergoes the usual secondary reactions, whereas thermal cracking produces relatively little benzene and the side chains crack indiscriminately. Unsubstituted aromatics are very stable under the usual cracking conditions. The results of Greensfelder, Voge and Good ¹¹⁶ showed that longer side chains increase the ease of cracking and that the presence of tertiary carbon atoms has the same effect in the aromatic group of hydrocarbons as in that of the paraffins.

Another interesting reaction which takes place is the disproportionation of methyl groups on aromatic rings. Hansford

et al¹¹⁷ reacted methyl benzenes at 510°C to 538°C on cracking catalysts and found that the main reaction was methyl transfer from one molecule to another leading to the formation of less and more highly substituted methylbenzenes than the initial compound. Xylenes disproportionated according to the equation



forming a range of trimethyl benzenes and toluene.

Isomerisation Reactions

Several types of isomerisation reactions occur under the conditions of catalytic cracking. They are commonly observed with olefins and aromatics which are invariably produced and the isomers tend towards equilibrium. Olefins are very readily isomerised and both the shifting of the double bond and chain branching occur readily and at the usual cracking temperatures between 400°C and 500°C. Double bond shift and cis-trans isomerisation can always be expected to be at equilibrium at these temperatures ¹¹⁸. Another example of chain branching isomerisation is that of ring expansion and contraction among cyclic olefins ¹¹⁹.

The shifting of methyl groups around aromatic rings has also been observed although this process usually requires more severe conditions than those outlined for the olefins. This reaction is closely related to the disproportionation reaction already mentioned and the interconversion of the xylene isomers has been the subject of most studies.¹¹⁶ The shift of a methyl group

from the α to the β position on a naphthalene nucleus occurs with great ease, however, and it seems as if bicyclic aromatics of this nature are much more readily activated than their monocyclic analogues.

Polymerisation, Condensation and Coke formation

Reaction of hydrocarbons on silica-alumina often results in some products which contain a larger number of carbon atoms than the starting material. Aromatics are prominent among such products, even in the cracking of simple paraffins, and the sequence of reactions leading to their formation is not well understood. Silica-alumina is active for the polymerisation of olefins at moderate temperatures and the polymerisation reactions of propylene and butenes on several catalysts have been reported by Thomas ¹²⁰. Prominent amounts of condensation products are obtained in the catalytic cracking of olefins and aromatics such as mesitylene and styrene.

Coking is due to the formation of hydrocarbons of very low volatility formed by condensation reactions, with the simultaneous elimination of hydrogen. The reaction products are strongly held on the catalyst surface and give the characteristic brown colour indicative of such processes. In many cases the formation of this coke deposit lowers the activity of the catalyst and many investigations have been carried out to discover the exact nature of this residue. Haldeman and Botty ¹²¹ suggested that the coke deposit had a pseudo-graphitic structure.

Dehydrogenation and Hydrogen Transfer

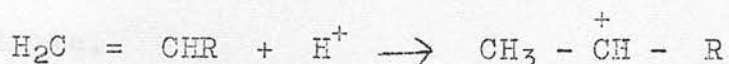
It is generally thought that silica-alumina is a poor dehydrogenation catalyst although it has been suggested ⁹⁵ that hydrogen can be abstracted from paraffins. However, under cracking conditions silica-alumina is quite a good hydrogen transfer catalyst leading to the presence of saturated paraffins of higher hydrogen to carbon ratio and lower carbon number than the initial reactant and aromatics of higher carbon number which are hydrogen deficient with respect to the starting material. This hydrogen transfer reaction is not of the same type as that which occurs on metals like platinum and it was found that the addition of hydrogen had the same effect as adding an inert diluent. Hydrogen transfer is greatly favoured by the addition of certain donor compounds, the most effective of which seem# to be large naphthalenes such as decalin, naphthene - aromatics such as tetralin or unsaturated compounds like cyclohexene.

1.4 The Carbonium Ion Theory of Reaction Mechanisms

It can be seen from the foregoing discussion that a remarkable number of reactions are possible on these oxide catalysts. The best theoretical explanation put forward so far, and the one that is most generally accepted, is that these reactions are all due to the formation of carbonium ions. This theory which is based on the acidic characteristics of the catalyst, and these have been clearly demonstrated, has the advantage that it relates these reactions to many well known reactions in other

acidic media and also explains most of the facts. Carbonium ions are electron deficient entities and the basic steps in their formation are believed to be the addition of a proton to an olefin or an aromatic molecule and the removal of a hydride ion from a saturated hydrocarbon.

Conceptually the formation of a carbonium ion is most easily represented as proton addition to an olefin bond:

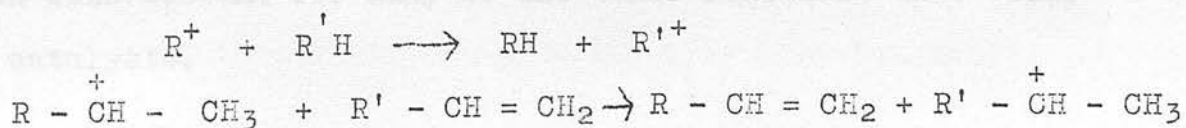


The carbonium ions are probably better regarded as polarized complexes rather than free ions, as they are associated with negative centres on the surface.

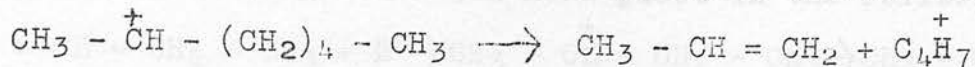
Certain rules governing the behaviour of carbonium ions have been developed on the basis of experimental and theoretical data. They are believed to be labile and to readily rearrange by shift of methyl groups and hydrogen ions. These shifts are commonly referred to as 1,2 - shifts and can be illustrated by equations of the type:



Because of their reactivity, it is believed that their formation is the slow step in many reactions. They can propagate the formation of new ions from other species by transfer of hydride ions or protons:



A large ion can split to form an olefin and a smaller ion:

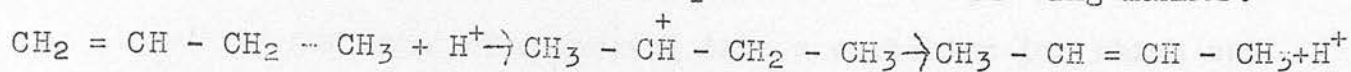


Splitting always occurs in the bond beta to the charged centre and this rule is known as the rule of β -scission, which also applies to 1,2 - shifts. The relative stabilities of carbonium ions decrease in the series tertiary, secondary, primary, ethyl and methyl. Where there is a chance of forming more than one ion the more stable one will predominate.

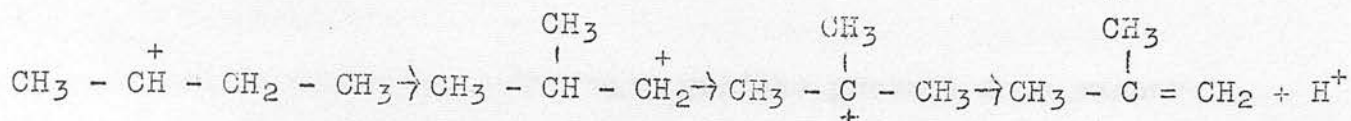
There is a certain amount of theoretical justification for the above hypotheses. The ease of rearrangement of carbonium ions is understandable from the postulation of a localized positive charge which attracts the electrons from neighbouring bonds, thereby lowering the activation energy required to break these bonds. The β -scission rule represents the only manner of molecular splitting that will give a neutral olefin and a smaller carbonium ion without the rearrangement of carbon or hydrogen atoms during the process. Since only electrons are shifted the principle of least motion for elementary chemical reactions is observed.

Beta splitting, in conjunction with the relative energies of the different carbonium ions and the ease of hydrogen shift, gives a very good explanation for the difficulty of forming methane, ethane and ethylene in catalytic cracking. The carbonium ion theory can also account for many of the other reactions that occur on these catalysts.

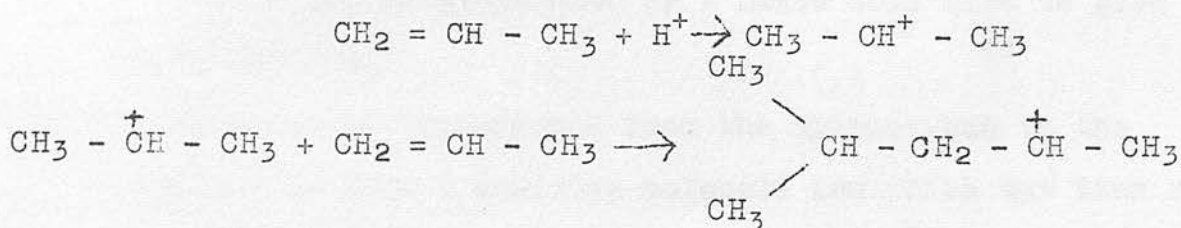
Double bond migration can take place in the following manner:



Methyl and hydrogen shifts can lead to chain branching:



Polymerisation takes place by the formation of an ion from the initial olefin followed by the addition of the ion to a second olefin molecule:

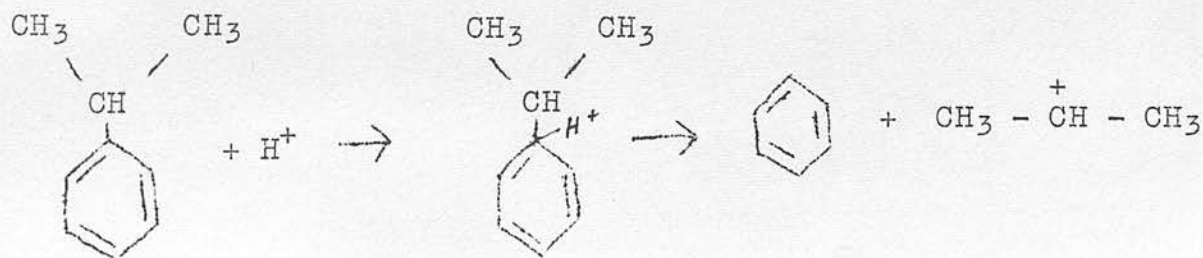


This reaction can proceed further to form high molecular weight polymers or the reaction can be terminated by neutralisation of the carbonium ion to form a paraffin or olefin by hydride ion abstraction from another molecule or loss of a proton. The cracking of olefins is essentially the reverse of polymerisation.

While the carbonium ion theory is very satisfactory for explaining reactions of olefins on cracking catalysts opinions differ considerably where paraffins are concerned. The initial adsorption process for saturated hydrocarbons has been explained in several ways and the variations of opinion are mainly due to the controversial issue of the nature of the active sites. The following are some of the mechanisms which have been suggested.

- (1) A small amount of olefin is formed or is present as an impurity and this is converted into a carbonium ion which can abstract a hydride ion from the paraffin thus setting up a chain reaction.
- (2) Paraffin molecules react with surface protons in a manner which gives carbonium ions and molecular hydrogen.
- (3) A catalyst proton attacks a paraffin molecule splitting it into a smaller paraffin and a carbonium ion.
- (4) A hydride ion is abstracted by a Lewis acid site to give a carbonium ion.
- (5) An electron is transferred from the hydrocarbon to the catalyst to form a positive molecule ion which may then react to form a carbonium ion ¹²².

The formation of carbonium ions from naphthenes evidently occurs in the same manner as with paraffins and here again the difficulty in deciding the nature of the initial adsorption step arises. There has also been some doubt about the mechanism of adsorption and cracking of alkyl aromatics. Vogt ¹²³ and later workers have postulated that an attack of the aromatic ring by a proton is involved as in the following example



In summary it can be said that the carbonium ion theory satisfactorily explains the chief characteristics of catalytic cracking. There are some features, however, which require further explanation such as the dehydrogenation to molecular hydrogen observed with larger naphthenes, which implies that silica-alumina catalysts have a small dehydrogenation activity like that displayed by γ alumina.

The use of deuterated catalysts for studying the reactions of hydrocarbons has provided strong support for the carbonium ion theory. It was found that hydrogen exchange took place at temperatures lower than those required for cracking to occur and this demonstrated the ability of the catalyst to add to or remove hydrogen from hydrocarbon molecules as required by the carbonium ion theory. The exchange reactions brought about by these catalysts were very similar to those carried out in homogeneous acid solutions again demonstrating the ionic nature of the reaction intermediates. A fuller discussion of the details of these exchange experiments will be given along with the discussion of the present work on these catalysts.

Experimental2.1 MaterialsCatalysts

Details of the catalysts used are given in Table 2.1. The two silica-alumina catalysts (designated I and II) were commercial samples supplied by the Agricultural Division of I.C.I. The alumina sample contained 97% gibbsite and 3% bayerite and was obtained from Peter Spence and Sons Ltd.

Silica alumina II was prepared by precipitation from Aluminium nitrate and Silicon tetrafluoride by treatment with ammonia, the final catalyst containing only traces of chloride. No details were obtainable on the preparation of silica alumina I.

Table 2.1 Nature of the Catalysts

Catalyst	Surface Area (m ² /g)	Percentage alumina	Impurities (%)	
			Na ₂ O	Fe
Silica-alumina I	470	13	~0.02	~0.043
Silica-alumina II	118	45.1	~0.15	~0.1
Alumina	370	100	<0.001	<0.002

The alumina sample was obtained by electrochemical attack on high purity aluminium metal as described in Patent B.P. 880580. Apart from the data in table 2.1 this sample has the following characteristics

Structure after calcination at 420°C	- Chi alumina (Stumpf)
particle size	- 20-600 millimicrons
Silica	- <0.002%
HCOOH	- <0.01%
NH ₃	- <0.001%

The analyses quoted above and in Table 2.1 were supplied with the catalysts except for the surface areas of silica-alumina I and alumina. The surface areas of these catalysts were measured by nitrogen adsorption using the method of Brunauer, Emmett and Teller. Areas were determined after evacuating the samples for 12 hours at 520°C in order to obtain a measure of the surface area under reaction conditions.

Chemicals

Benzene and Toluene were AnalaR grade samples which were dried over Linde 5A molecular sieve and purified by vacuum distillation before use.

m-Xylene was obtained as a 99.91% sample from the Chemical Standards Division of the N.P.L. and was used without further purification.

Deuterium (99.5%) was obtained from the Matheson Company and purified by diffusion through a palladium thimble followed

by two liquid nitrogen traps in series.

Oxygen was obtained from the British Oxygen Company and was dried by passage through a liquid nitrogen trap.

The purified oxygen and deuterium were stored in gas bulbs. The hydrocarbons were kept frozen in sample tubes and before use were thoroughly outgassed by repeated cycles freezing, pumping and thawing.

2.2 Exchange Procedure

Catalyst activation

The activation procedure used was the same for all catalysts. This involved heating the catalyst (0.1-0.3g) in the silica reaction vessel in oxygen (100 torr) for three hours at 520°C followed by evacuation for 10 minutes and a second oxygen treatment for a further three hours. Finally the catalyst was outgassed for 12 hours at 520°C at 10^{-6} torr. The purpose of this oxygen treatment was to burn off any carbonaceous residues on the catalyst surface and although the same sample was used for a series of runs the whole activation procedure was repeated before carrying out each experiment.

Reaction Procedure

After the catalyst had been activated, the reaction vessel was cooled and the preprepared gas mixture expanded from the mixing volume into the reaction vessel. The standard mixture of reactants consisted of 3 torr hydrocarbon and 60 torr

deuterium in the mixing volume and in order to minimise solution of the hydrocarbon in the tap grease the mixture was made up only 15 to 30 minutes before use. The number of molecules of hydrocarbon admitted to the reaction vessel was 1.06×10^{19} when the reaction vessel was at 20°C and 0.85×10^{19} when it was maintained at 120°C . After admission of the gas mixture (at 20°C for Alumina and silica-alumina II and 120°C for silica-alumina I). the catalyst temperature was raised until reaction was occurring at a measurable rate. The exchange reaction was monitored by the mass spectrometer and was measured at two or more temperatures during the run.

2.3 Mass Spectrometric analysis

In the experiments with benzene and toluene mass spectrometric analyses were carried out with an ionising beam of 13V electrons in order to keep the amount of fragmentation at a reasonably low value and also obtain enough sensitivity to enable the various amounts of isotopic hydrocarbons to be accurately measured. With m-xylene it was found that best results were obtained using 17V electrons.

Parent ions in the mass ranges 78-84, 92-100 and 106-116 were used to determine the composition of the various isotopic benzenes, toluenes and m-xylenes respectively. Scans of these regions of the spectrum were taken at suitable time intervals according to the reaction rate and analysed as described in Part I Chapter 4 of this thesis.

Isotope Corrections

Corrections were made to the observed peak heights to allow for the presence of naturally occurring ^{13}C only since the corrections for naturally occurring deuterium were negligible compared with the experimental error in peak height determination. The values of the isotope corrections used were those determined experimentally for the 'neat' hydrocarbon. Corrections were made for the possibility of having one and two ^{13}C in a molecule and the values used agreed well with those calculated theoretically. Table 2.2 shows the magnitude of the corrections used in this work. For comparison Table 2.3 shows the complete theoretical contribution of all of the isotopic m-xylenes or any compound of the formula C_8H_{10} to the peaks at one and two mass units higher. These Tables were calculated using

$$\frac{100 \text{ } ^{13}\text{C}}{^{13}\text{C} + ^{12}\text{C}} = 1.0806$$

$$\frac{100 \text{ D}}{\text{D} + \text{H}} = 0.016003$$

where P_M , P_{M+1} , P_{M+2} are the same conventions as used in Part I Chapter IV.

Table 2.2 Isotope corrections for 'neat' hydrocarbons

hydrocarbon	formula	^{13}C		^{13}C and D		Correction used	
		$100 \frac{P_{M+1}}{P_M}$	$100 \frac{P_{M+2}}{P_M}$	$100 \frac{P_{M+2}}{P_M}$	$100 \frac{P_{M+2}}{P_M}$	$100 \frac{P_{M+1}}{P_M}$	$100 \frac{P_{M+2}}{P_M}$
benzene	C_6H_6	6.484	0.1752	6.580	0.1814	6.6	-
toluene	C_7H_8	7.564	0.2452	7.692	0.2550	7.6	0.2
m-xylene	C_8H_{10}	8.645	0.3270	8.805	0.3409	8.8	0.3

Table 2.3 Statistical isotope corrections for m-xylene to account for the presence of naturally occurring ^{13}C and D.

Mass	Compound	$100 \frac{P_{M+1}}{P_M}$	$100 \frac{P_{M+2}}{P_M}$
116	C_8D_{10}	8.645	0.327
115	C_8HD_9	8.661	0.328
114	$\text{C}_8\text{H}_2\text{D}_8$	8.677	0.330
113	$\text{C}_8\text{H}_3\text{D}_7$	8.693	0.331
112	$\text{C}_8\text{H}_4\text{D}_6$	8.709	0.333
111	$\text{C}_8\text{H}_5\text{D}_5$	8.725	0.334
110	$\text{C}_8\text{H}_6\text{D}_4$	8.741	0.335
109	$\text{C}_8\text{H}_7\text{D}_3$	8.757	0.337
108	$\text{C}_8\text{H}_8\text{D}_2$	8.773	0.338
107	$\text{C}_8\text{H}_9\text{D}$	8.789	0.340
106	C_8H_{10}	8.805	0.341
105	C_8H_9	8.789	0.339
104	C_8H_8	8.773	0.338

Fragmentation Corrections

A mass spectrum of the aromatic molecule was taken at the beginning of each experiment before reaction temperature had been reached or before an appreciable amount of the hydrocarbon had reacted and from this was determined the extent of fragmentation of the 'neat' hydrocarbon. Although for each experiment on a particular molecule the source parameters of the mass spectrometer were kept constant it was found that the amount of fragmentation varied from one experiment to another and hence a new fragmentation pattern was determined before each run and only used for calculations on that particular experiment. Typical fragmentation patterns of the three aromatic molecules used are given in Table 2.4.

Table 2.4 The fragmentation patterns of aromatic molecules

Molecule	electron volts	f_1	f_2	f_3
benzene	13	2.0	0.3	1.0
toluene	13	27.0	0.3	1.0
m-xylene	17	14.0	0.4	3.0

The values quoted are percentages of the parent peak and show the chances of losing one, two or three hydrogen (or deuterium) atoms (f_1 , f_2 and f_3 respectively) from the parent molecule. In all cases only the fragments shown above were of importance in analysis of the results.

Calculation of the fragmentation of the other isotopic hydrocarbons were evaluated on a statistical basis which involved determining the chance of losing the appropriate number of hydrogen and deuterium atoms from the parent molecule assuming an equal chance for the loss of a deuterium or hydrogen atom. The method is illustrated in Table 2.5 for the species $C_8H_6D_4$. By carrying out this procedure for all the isotopic species the statistical factors in Tables 2.6, 2.7 and 2.8 were obtained. By inserting the numerical values of f_1 , f_2 and f_3 , obtained at the beginning of an experiment, into these tables the contribution of any peak to another peak due to fragmentation could be calculated.

Table 2.5 Calculation of the fragmentation scheme for $C_8H_6D_4$

Number of mass units lost	Method of loss	Chance of loss taking place
-1	H	$\frac{6}{10} f_1$
-2	D H H	$\frac{4}{10} f_1$ $(\frac{6}{10} \times \frac{5}{9}) f_2$
-3	HD or DH HHH	$2 (\frac{6}{10} \times \frac{4}{9}) f_2$ $(\frac{6}{10} \times \frac{5}{9} \times \frac{4}{8}) f_3$
-4	DD HHD or HDH or DHH	$(\frac{4}{10} \times \frac{3}{9}) f_2$ $3 (\frac{6}{10} \times \frac{5}{9} \times \frac{4}{8}) f_3$
-5	HDD DHD DDH	$3 (\frac{6}{10} \times \frac{4}{9} \times \frac{3}{8}) f_3$
-6	DDD	$(\frac{4}{10} \times \frac{3}{9} \times \frac{2}{8}) f_3$

Table 2.6 Statistical weighting for fragmentation correction for benzene

Compound	Mol. wt.	Reduction in mass					
		-1	-2	-3	-4	-5	-6
C_6D_6	84	-	f_1	-	f_2	-	f_3
$C_6H_5D_5$	83	$\frac{1}{6} f_1$	$\frac{5}{6} f_1$	$\frac{12}{30} f_2$	$\frac{20}{30} f_2$	$\frac{60}{120} f_3$	$\frac{60}{120} f_3$
$C_6H_4D_4$	82	$\frac{2}{6} f_1$	$\frac{4}{6} f_1 + \frac{2}{30} f_2$	$\frac{16}{30} f_2$	$\frac{12}{30} f_2 + \frac{16}{120} f_3$	$\frac{72}{120} f_3$	$\frac{24}{120} f_3$
$C_6H_3D_3$	81	$\frac{3}{6} f_1$	$\frac{3}{6} f_1 + \frac{6}{30} f_2$	$\frac{18}{30} f_2 + \frac{6}{120} f_3$	$\frac{6}{30} f_2 + \frac{54}{120} f_3$	$\frac{54}{120} f_3$	$\frac{6}{120} f_3$
$C_6H_2D_2$	80	$\frac{4}{6} f_1$	$\frac{2}{6} f_1 + \frac{12}{30} f_2$	$\frac{16}{30} f_2 + \frac{24}{120} f_3$	$\frac{2}{30} f_2 + \frac{72}{120} f_3$	$\frac{24}{120} f_3$	-
$C_6H_5D_1$	79	$\frac{5}{6} f_1$	$\frac{1}{6} f_1 + \frac{20}{30} f_2$	$\frac{10}{30} f_2 + \frac{60}{120} f_3$	$\frac{60}{120} f_3$	-	-
C_6H_6	78	f_1	f_2	f_3	-	-	-

26 Table 2.7 Statistical weighting factors for fragmentation corrections for toluene

Compound	Mol. wt.	Reduction in mass					
		-1	-2	-3	-4	-5	-6
C ₇ D ₈	100	-	f ₁	-	f ₂	-	f ₃
C ₇ H ₇ D ₇	99	$\frac{1}{8} f_1$	$\frac{7}{8} f_1$	$\frac{14}{56} f_2$	$\frac{42}{56} f_2$	$\frac{126}{336} f_3$	$\frac{210}{336} f_3$
C ₇ H ₆ D ₆	98	$\frac{2}{8} f_1$	$\frac{5}{8} f_1 + \frac{2}{56} f_2$	$\frac{24}{56} f_2$	$\frac{30}{56} f_2 + \frac{36}{336} f_3$	$\frac{180}{336} f_3$	$\frac{120}{336} f_3$
C ₇ H ₅ D ₅	97	$\frac{3}{8} f_1$	$\frac{5}{8} f_1 + \frac{6}{56} f_2$	$\frac{30}{56} f_2 + \frac{6}{336} f_3$	$\frac{20}{56} f_2 + \frac{90}{336} f_3$	$\frac{180}{336} f_3$	$\frac{60}{336} f_3$
C ₇ H ₄ D ₄	96	$\frac{4}{8} f_1$	$\frac{4}{8} f_1 + \frac{12}{56} f_2$	$\frac{32}{56} f_2 + \frac{24}{336} f_3$	$\frac{12}{56} f_2 + \frac{144}{336} f_3$	$\frac{144}{336} f_3$	$\frac{24}{336} f_3$
C ₇ H ₃ D ₃	95	$\frac{5}{8} f_1$	$\frac{3}{8} f_1 + \frac{20}{56} f_2$	$\frac{30}{56} f_2 + \frac{60}{336} f_3$	$\frac{6}{56} f_2 + \frac{180}{336} f_3$	$\frac{90}{336} f_3$	$\frac{6}{336} f_3$
C ₇ H ₂ D ₂	94	$\frac{6}{8} f_1$	$\frac{2}{8} f_1 + \frac{30}{56} f_2$	$\frac{24}{56} f_2 + \frac{120}{336} f_3$	$\frac{2}{56} f_2 + \frac{180}{336} f_3$	$\frac{36}{336} f_3$	-
C ₇ H ₁ D ₁	93	$\frac{7}{8} f_1$	$\frac{1}{8} f_1 + \frac{42}{56} f_2$	$\frac{2}{56} f_2 + \frac{210}{336} f_3$	$\frac{126}{336} f_3$	-	-
C ₇ H ₈	92	f ₁	f ₂	f ₃	-	-	-

Table 2.8 Statistical weighting factors for fragmentation corrections for *m*-xylene

Compound	Mol. wt	Reduction in mass					
		-1	-2	-3	-4	-5	-6
C ₈ H ₁₀ D ₁₀	116	-	f ₁	-	f ₂	-	f ₃
C ₈ H ₉ D ₉	115	$\frac{1}{10} f_1$	$\frac{9}{10} f_1$	$\frac{18}{90} f_2$	$\frac{72}{90} f_2$	$\frac{216}{720} f_3$	$\frac{504}{720} f_3$
C ₈ H ₈ D ₈	114	$\frac{2}{10} f_1$	$\frac{8}{10} f_1 + \frac{2}{90} f_2$	$\frac{32}{90} f_2$	$\frac{36}{90} f_2 + \frac{48}{720} f_3$	$\frac{336}{720} f_3$	$\frac{336}{720} f_3$
C ₈ H ₇ D ₇	113	$\frac{3}{10} f_1$	$\frac{7}{10} f_1 + \frac{6}{90} f_2$	$\frac{42}{90} f_2 + \frac{6}{720} f_3$	$\frac{12}{90} f_2 + \frac{126}{720} f_3$	$\frac{378}{720} f_3$	$\frac{210}{720} f_3$
C ₈ H ₆ D ₆	112	$\frac{4}{10} f_1$	$\frac{6}{10} f_1 + \frac{12}{90} f_2$	$\frac{48}{90} f_2 + \frac{24}{720} f_3$	$\frac{30}{90} f_2 + \frac{216}{720} f_3$	$\frac{360}{720} f_3$	$\frac{120}{720} f_3$
C ₈ H ₅ D ₅	111	$\frac{5}{10} f_1$	$\frac{5}{10} f_1 + \frac{20}{90} f_2$	$\frac{50}{90} f_2 + \frac{60}{720} f_3$	$\frac{20}{90} f_2 + \frac{300}{720} f_3$	$\frac{300}{720} f_3$	$\frac{60}{720} f_3$
C ₈ H ₄ D ₄	110	$\frac{6}{10} f_1$	$\frac{4}{10} f_1 + \frac{30}{90} f_2$	$\frac{48}{90} f_2 + \frac{120}{720} f_3$	$\frac{12}{90} f_2 + \frac{360}{720} f_3$	$\frac{216}{720} f_3$	$\frac{24}{720} f_3$
C ₈ H ₃ D ₃	109	$\frac{7}{10} f_1$	$\frac{3}{10} f_1 + \frac{42}{90} f_2$	$\frac{42}{90} f_2 + \frac{210}{720} f_3$	$\frac{6}{90} f_2 + \frac{378}{720} f_3$	$\frac{126}{720} f_3$	$\frac{6}{720} f_3$
C ₈ H ₂ D ₂	108	$\frac{8}{10} f_1$	$\frac{2}{10} f_1 + \frac{56}{90} f_2$	$\frac{32}{90} f_2 + \frac{336}{720} f_3$	$\frac{2}{90} f_2 + \frac{336}{720} f_3$	$\frac{48}{720} f_3$	-
C ₈ H ₁ D ₁	107	$\frac{9}{10} f_1$	$\frac{1}{10} f_1 + \frac{72}{90} f_2$	$\frac{18}{90} f_2 + \frac{504}{720} f_3$	$\frac{216}{720} f_3$	-	-
C ₈ H ₁₀	106	f ₁	f ₂	f ₃	-	-	-

These corrections are only approximate since the chance of loss of a hydrogen or deuterium atom may not be exactly the same. Perhaps a more serious error occurs in the case of toluene and m-xylene where the fragment ions may not occur by a random loss of H or D, since the CH or CD bonds in the side groups are weaker than those in the ring positions. This may be important at ionising beam voltages just above the appearance potential of the parent ion but in the present work the results show that any errors arising from these sources are small.

By the use of the above isotope and fragmentation corrections the distribution of the various isotopic hydrocarbons at known times and temperatures were calculated from the observed peak heights of the mass spectrometer output and Arrhenius parameters calculated as described previously.

2.4 Gas Chromatographic analyses

The Gas chromatographic analyses were carried out using a 12 ft. column containing a packing (DE 210 LS 63547) from Perkin-Elmer and a flame ionisation detector. The column consisted of four pyrex tubes of approximately 4 mm. diameter joined by short pieces of 2 mm. capillary U tubing so that it could be inserted into a glass oven. It was attached to the carrier gas supply and the detector through two glass/metal seals. The packing was of silicone oil MS 555, Bentone 34 and 80-100 mesh Chromosorb W in the ratios $11\frac{1}{2}:11\frac{1}{2}:77$. It was found that a column containing 14 gms. of this packing when

operated at 100°C with nitrogen as carrier gas at an inlet pressure of 11 lbs./sq. inch gave a flow rate of 30 mls./min. (soap bubble meter) at the outlet and was capable of separating the isomeric xylenes. Typical retention times for the hydrocarbons investigated are given in Table 2.9.

Table 2.9. Retention times for the Gas Chromatography apparatus

hydro-carbon	Pentane	Benzene	Toluene	p-xylene	m-xylene	o-xylene	mesitylene
Retention time (mins)	2	8	14	24.5	28	30.5	48

The retention times for the aromatic hydrocarbons were measured by injecting pure samples of the liquid into the gas stream. The pentane used for diluting the hydrocarbons was found to contain only trace amounts of hydrocarbons higher than C₅. A typical trace for a sample containing equal amounts of benzene, toluene and m-xylene dissolved in pentane is shown in Figure 2.1 along with the resolution obtained for a mixture of the three isomeric xylenes

Samples were obtained for gas chromatographic analyses by admitting the gas mixture containing $\sim 10^{19}$ molecules hydrocarbon

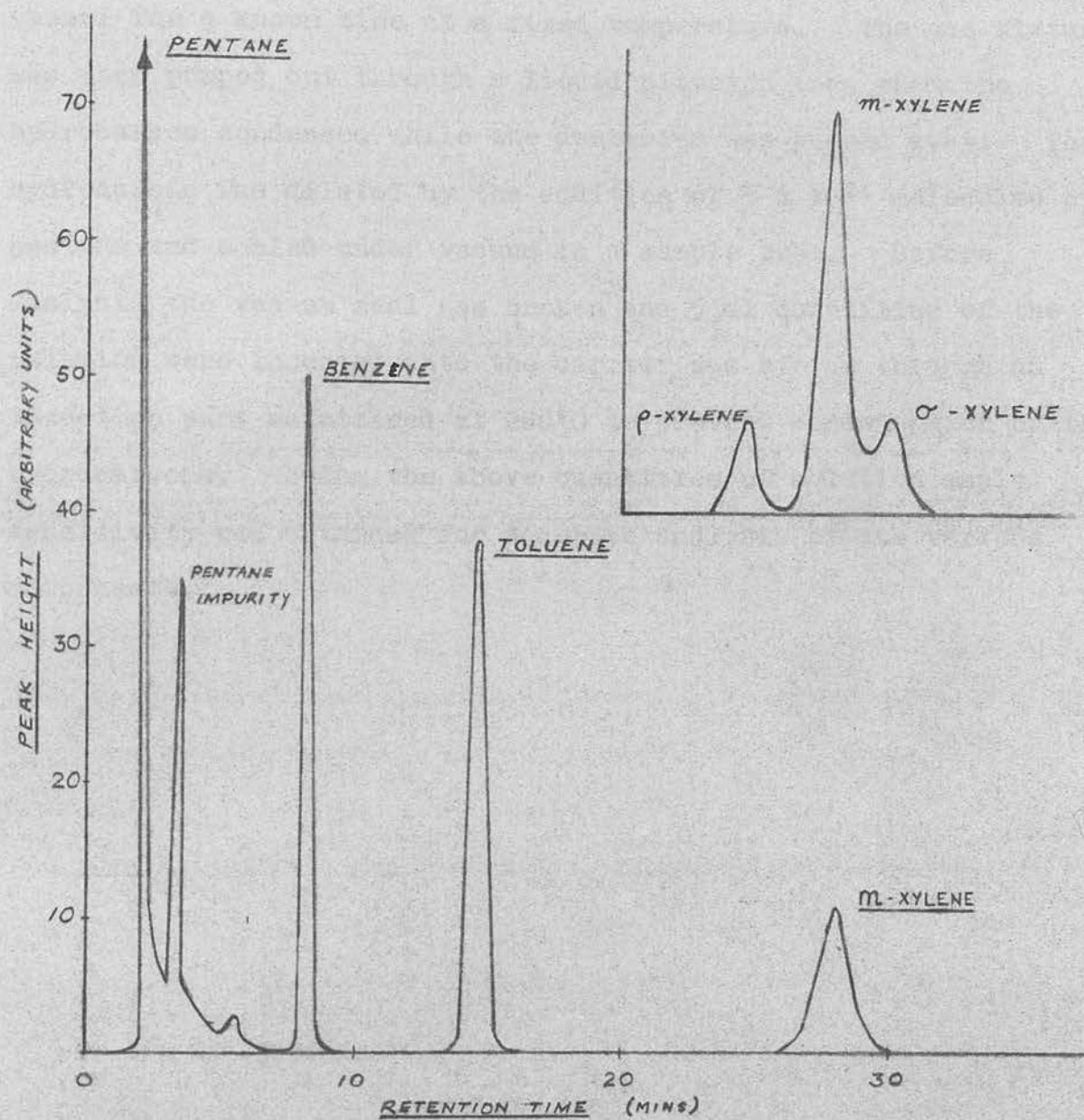


FIGURE 2.1

SEPARATION OF BENZENE, TOLUENE AND m-XYLENE
(INSERT o, m AND p XYLENES) ACHIEVED BY
GAS CHROMATOGRAPH.

and 2×10^{20} molecules deuterium to the catalyst in the reaction vessel for a known time at a fixed temperature. The gas mixture was then pumped out through a liquid nitrogen trap where the hydrocarbon condensed while the deuterium was pumped away. The hydrocarbon was diluted by the addition of 3×10^{21} molecules of pentane and sealed under vacuum in a sample tube. Before analysis the vacuum seal was broken and $5 \mu\text{l}$ quantities of the solution were injected into the carrier gas stream through an injection port maintained at 200°C to prevent condensation of the hydrocarbons. Using the above quantities of solution ample sensitivity was obtained for accurate analysis of the various components.

percentage of isotopic species contained in the sample at time t , ϕ , is the equilibrium value of ϕ . The initial rate of disappearance of the light hydrocarbon k_1 was obtained from equation (2)

$$\log_{10} \phi_0 = -k_1 / 2.303 = \log_{10} (100) \quad (2)$$

The ratio k_1/k_2 gave the average number of deuterium atoms entering each molecule in the initial stages of the reaction.

For the toluene and *m*-xylene samples which contained different types of hydrogen atoms, which reacted at different rates, the plot according to equation (1) was not linear although the initial and final portions approached a straight line with different slopes. Under these circumstances modified equations similar to equation (1) had to be used to determine the rates of reaction.

CHAPTER 3

Results3.1 Method of analysing experimental data

The methods used for determining the rate of exchange of the various types of hydrogen atoms in the hydrocarbon molecules were similar to those described by Harper, Siegel and Kemball ⁵¹. For benzene, where all the hydrogen atoms were replaced at the same rate, the course of the exchange was given by equation (1)

$$\log_{10} (\phi_{\infty} - \phi) = -k_{\phi}t/2.303 \phi_{\infty} + \log_{10} \phi_{\infty} \quad (1)$$

where k_0 is the initial rate of entry of deuterium atoms into 100 molecules of hydrocarbon and $\phi = \sum i d_i$, d_i being the percentage of isotopic species containing i deuterium atoms at time t ; ϕ_{∞} is the equilibrium value of ϕ . The initial rate of disappearance of the light hydrocarbon k_0 was obtained from equation (2)

$$\log_{10} d_0 = -k_0t/230.3 + \log_{10} (100) \quad (2)$$

The ratio k_{ϕ}/k_0 gave the average number of deuterium atoms entering each molecule in the initial stages of the reaction.

For the toluene and m-xylene molecules which contained different types of hydrogen atoms, which reacted at different rates, the plot according to equation (1) was not linear although the initial and final portions approximated to straight lines with different slopes. Under these circumstances modified equations similar in form to equation (1) had to be used to determine the rates of reaction.

If there are two groups of hydrogen atoms, A and B, reacting at different rates k_{ϕ} and k_o will be composite terms of the form:

$$k_{\phi} = k_{\phi A} + k_{\phi B} \quad (3)$$

$$k_o = k_{oA} + k_{oB} \quad (4)$$

where k_A and k_B represent the rate of exchange of the first and second group of atoms respectively ($k_A > k_B$). If k_A is much larger than k_B the rate of exchange of the second group of atoms can be measured after the first group has reacted. By defining quantities ϕ_B and x_B by the relations:

$$\phi_B = 100 \times \frac{\sum_a^n (i-a) di}{\sum_a^n di} \quad (5)$$

$$\text{and } x_B = 100 d_a / \sum_a^n di \quad (6)$$

where a is the number of hydrogen atoms in the first groups and n is the total number of hydrogens in the molecule, and using these in the equations:

$$\log_{10} (\phi_{B\infty} - \phi_B) = -k_{\phi B} t / 2.303 \phi_{B\infty} + \log_{10} \phi_{B\infty} \quad (7)$$

$$\text{and } \log_{10} x_B = -k_{oB} t / 2.303 (100 - x_{B\infty}) + \log_{10} (100 - x_{B\infty}) \quad (8)$$

the course of exchange of group B hydrogens can be measured.

Care was required in selecting the values to be used for $\phi_{B\infty}$ and $x_{B\infty}$. If it had been possible to measure the total concentration of deuterium in the positions corresponding to group B it would have been correct to determine $\phi_{B\infty}$ by the relationship:

$$\phi_{B\infty} = \frac{B}{B + A} \phi_{\infty} \quad (9)$$

where ϕ_{∞} is the equilibrium value of ϕ for the molecule as a whole. However, it was only possible by these methods to measure the exchange in the group B positions in molecules which had already exchanged all their group A hydrogen atoms and so a smaller value of $\phi_{B\infty}$ was appropriate. For any molecule containing n hydrogen atoms and a gas mixture of P_{D_2} and P_{HC} pressures of deuterium and hydrocarbon respectively, the final equilibrium distribution of isotopic hydrocarbons can be calculated knowing the average number of deuterium atoms per 100 molecules of hydrocarbon at equilibrium, which can be calculated statistically using the expression:

$$\phi_{\infty} = 100 \times n \frac{(2 \times P_{D_2})}{(2P_{D_2} + n P_{HC})} \quad (10)$$

However, it was found that the experimental value for ϕ_{∞} was higher than that given by the above expression by about 10% and so the equilibrium distribution of all the isotopic species were calculated, by use of the binomial expansion, using a previously determined experimental value for ϕ_{∞} . The equilibrium values of $\phi_{B\infty}$ and $x_{B\infty}$ were then obtained by substituting these values into equations (5) and (6).

Values of $k_{\phi A}$ were determined by using ϕ_A defined as:

$$\phi_A = \sum_{i=1}^{i=a} i d_i + \cancel{na} \sum_{i=a+1}^{i=n} d_i \quad (11)$$

$\phi_{A\infty}$ was determined experimentally since equilibrium was obtained in this group before appreciable amounts of group B had reacted. The second term in equation (11) was thus small and was sometimes neglected. Values for $k_{\phi A}$ could then be obtained from equation (3) but since $k_{\phi\beta}$ was initially much smaller than $k_{\phi A}$, $k_{\phi A}$ was equated to k_{ϕ} directly. k_{oA} was obtained from equation (2).

The mean number of deuterium atoms replaced initially in each group were obtained from the relationships:

$$M_A = \frac{k_{\phi A}}{k_{oA}} \quad ; \quad M_B = \frac{k_{\phi B}}{k_{oB}} \quad (12)$$

3.2 Nature of the Exchange Reaction

It was found that the individual nature of exchange of the benzene, toluene and *m*-xylene molecules did not differ over the catalyst used. Figures 3.1, 3.2, and 3.3, showing how the various isotopic species of each hydrocarbon varied with time, demonstrate the typical way in which successive replacement of hydrogen by deuterium occurred on the silica-alumina II catalyst. Similar results were found with silica-alumina I and alumina the only difference being the temperature at which reaction took place.

The value of k_{ϕ}/k_o was found to be unity for each system showing that stepwise exchange with replacement of a single hydrogen atom at a time was occurring with each hydrocarbon over the three catalysts. On each catalyst the ring hydrogen

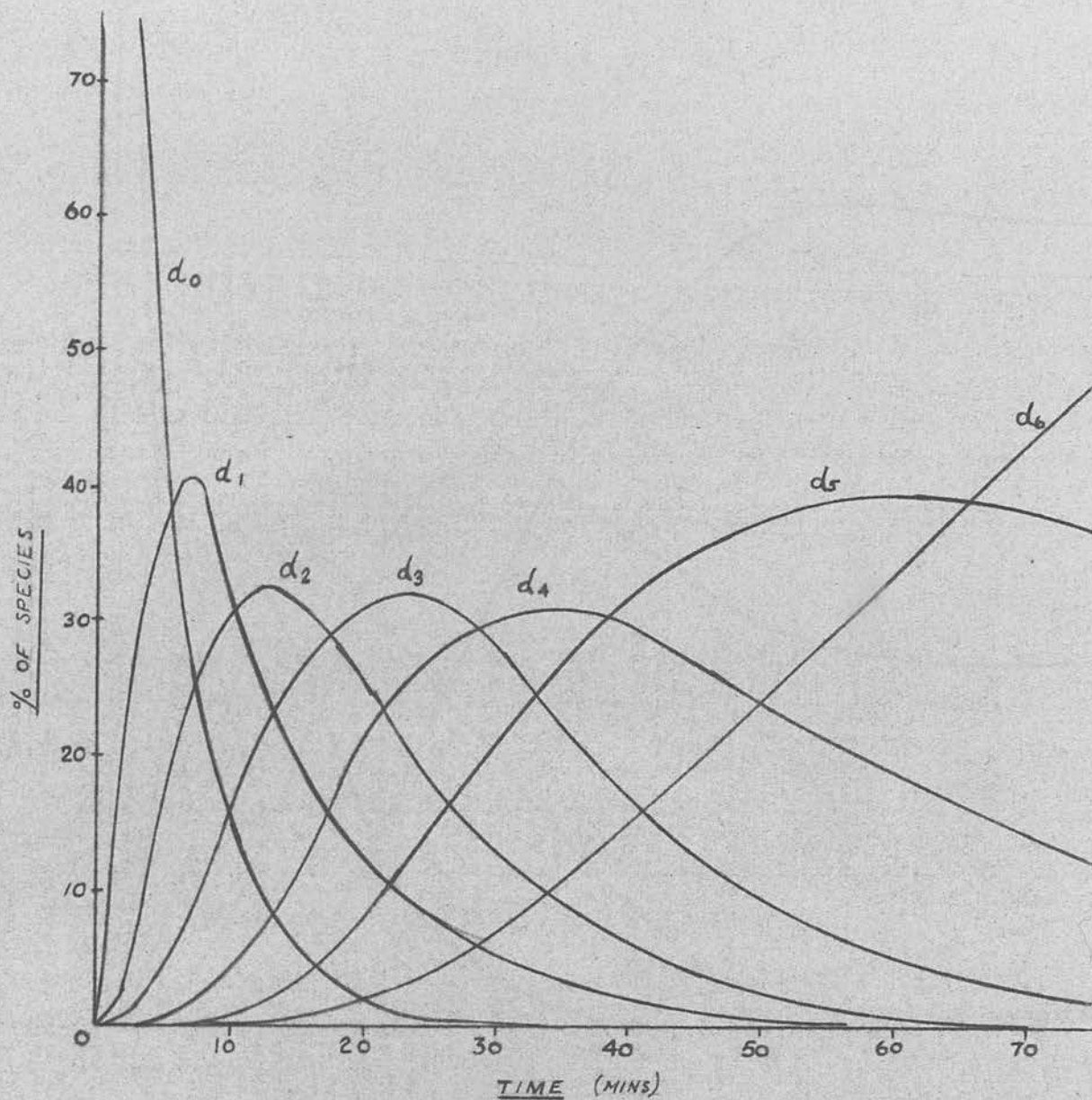


FIGURE 3.1
DISTRIBUTION OF ISOTOPIC BENZENES
PRODUCED DURING REACTION ON 0.05
GMS. SILICA-ALUMINA II AT 50°C.

$$P_{O_2}/P_{C_6H_6} = 20.0$$

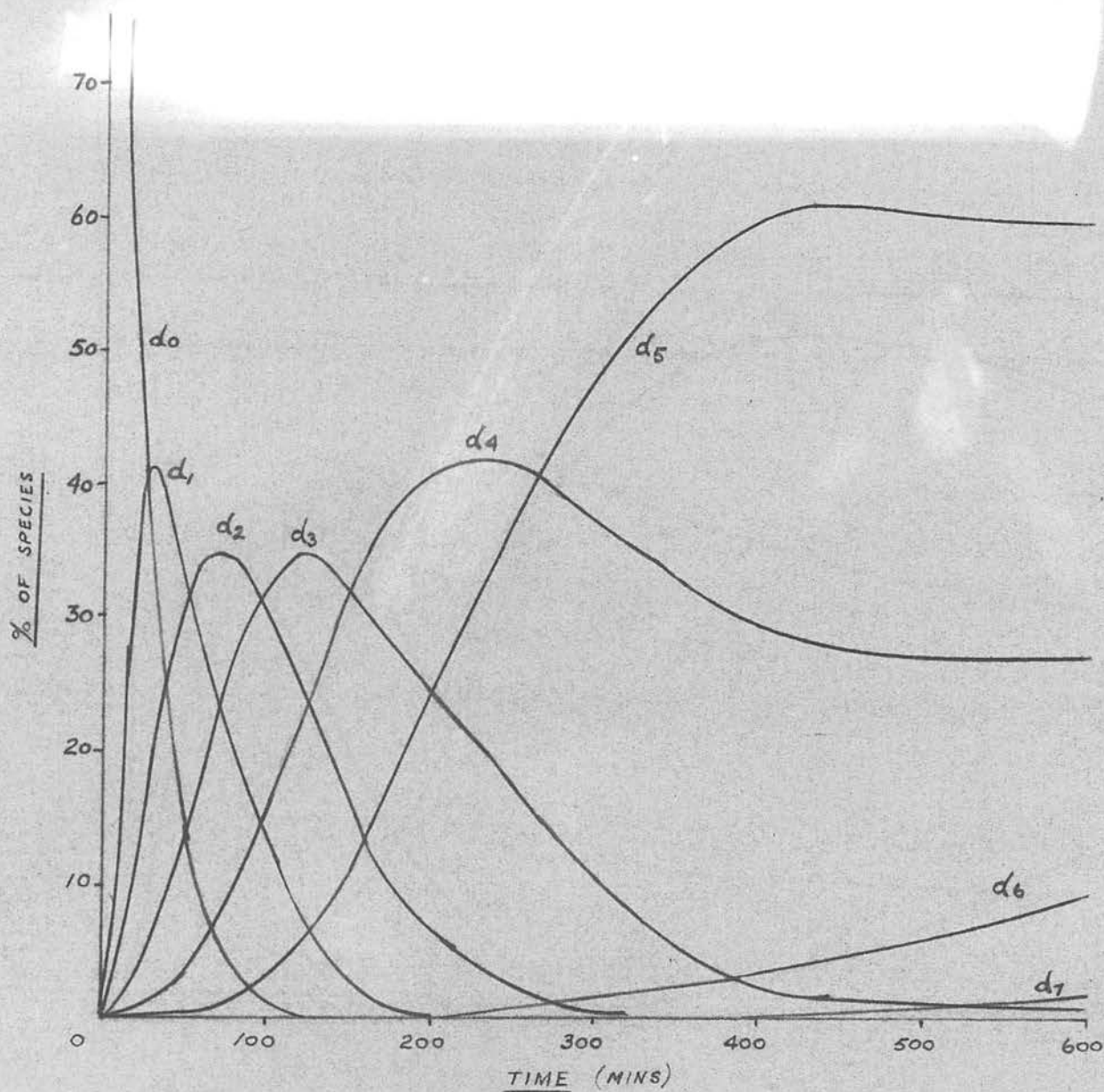


FIGURE 3.2

DISTRIBUTION OF ISOTROPIC TOLUENES
PRODUCED DURING REACTION ON 0.05
GMS. SILICA-ALUMINA II AT 23.5°C.

$$\frac{P_{D_2}}{P_{C_7H_8}} = 20.2$$

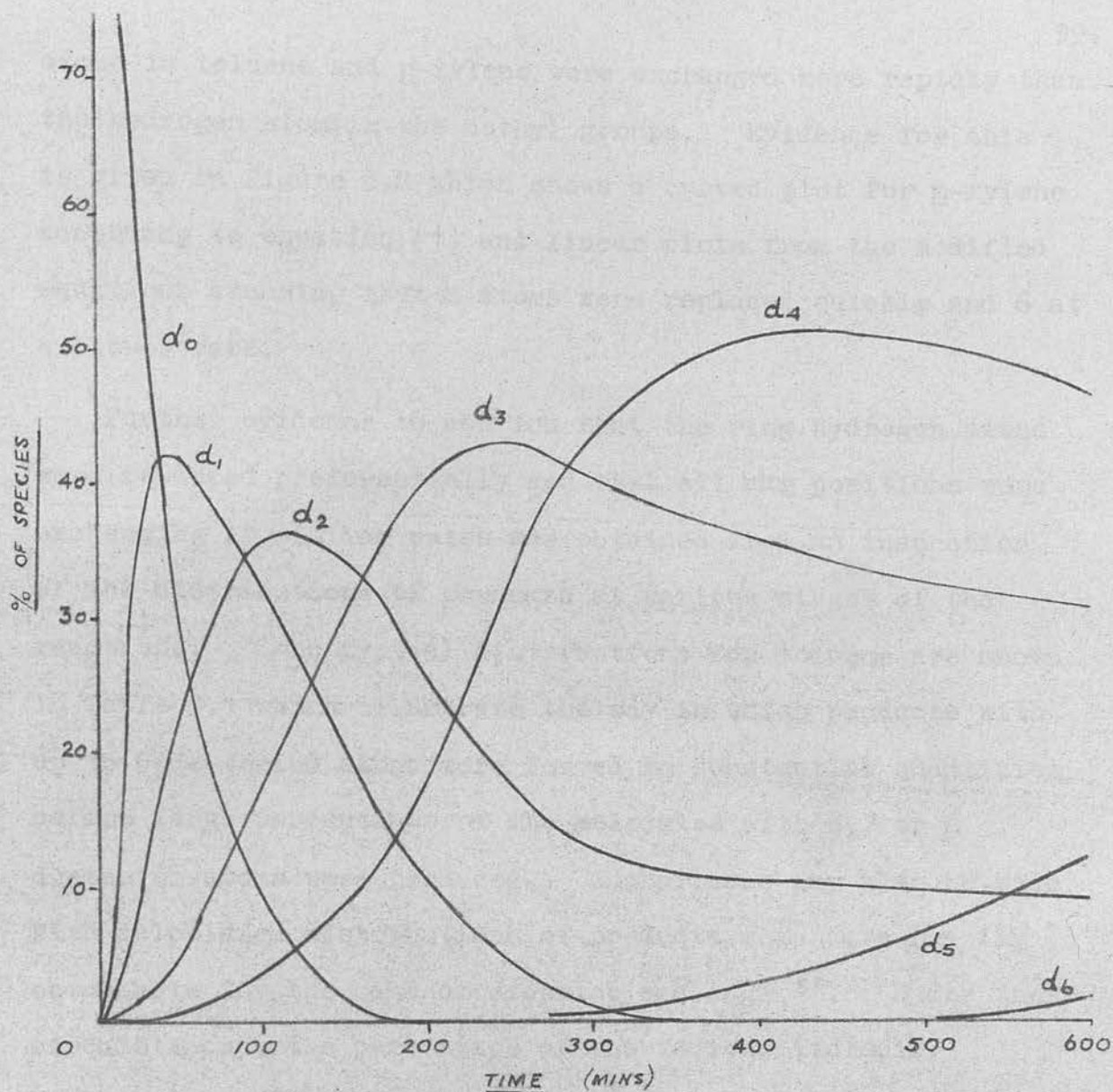


FIGURE 3.3

DISTRIBUTION OF ISOTOPIC m-XYLENES
PRODUCED DURING REACTION ON 0.05
GMS. SILICA-ALUMINA II AT 25°C.

$$\frac{P_{D_2}}{P_{C_7H_{10}}} = 19.6$$

atoms in toluene and m-xylene were exchanged more rapidly than the hydrogen atoms in the methyl groups. Evidence for this is given in Figure 3.4 which shows a curved plot for m-xylene according to equation (1) and linear plots from the modified equations assuming that 4 atoms were replaced quickly and 6 at a slower rate.

Further evidence to confirm that the ring hydrogen atoms were replaced preferentially and that all ring positions were exchanging at similar rates was obtained from an inspection of the distributions of products at various stages of the reactions. Some typical distributions for toluene are shown in Table 3.1 which illustrate the way in which products with up to 5 deuterium atoms were formed in substantial quantities before large percentages of the molecules with 6, 7 or 8 deuterium atoms were produced. Comparisons may also be made with calculated distributions of products which are readily obtainable for the case of stepwise exchange ³³. Under these circumstances, the percentage of the various isotopic hydrocarbons for a molecule in which all the hydrogen atoms are equally reactive may be derived at any stage of the reaction from the terms of the binomial expansion:

$$100 \left(\frac{100n - \phi t}{100n} + \frac{\phi t}{100n} \right)^n \quad (13)$$

where n is the number of exchangeable hydrogen atoms and ϕt is the value of ϕ at time t . The i th term, in the expansion then gives the theoretical percentage of d_i for the particular

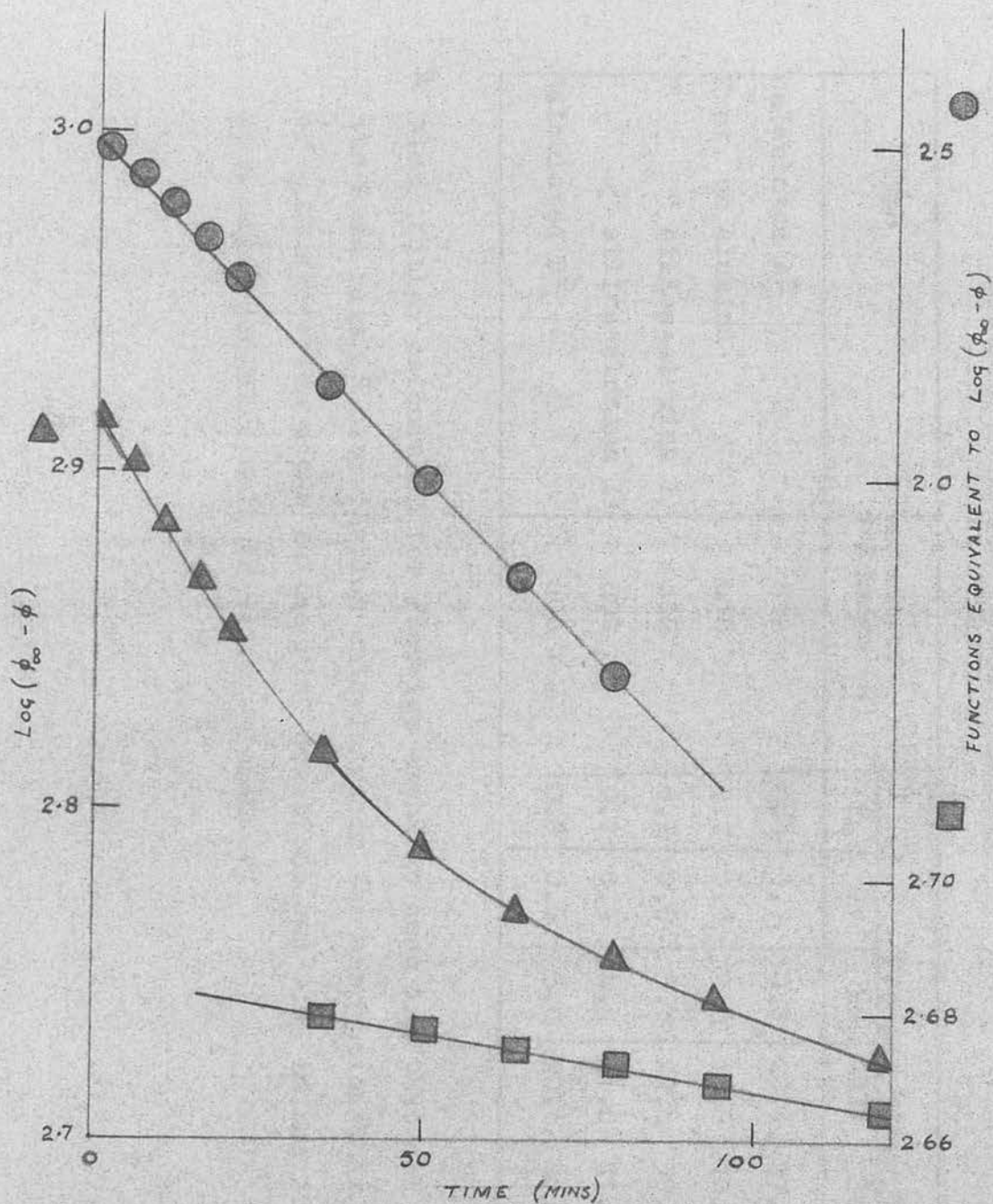


FIGURE 3.4

RATE PLOTS FOR THE EXCHANGE OF m-XYLENE ON SILICA-ALUMINA 1 AT 278°C : ▲ PLOT ACCORDING TO EQUATION (1) : ● USING A MODIFIED FORM OF EQUATION (1) ASSUMING 4 EXCHANGEABLE ATOMS : ■ THE CORRESPONDING PLOT FOR THE LAST 6 HYDROGEN ATOMS

Table 3.1 A comparison of experimental and calculated product distributions for toluene exchange

Type	Extent of exchange (ϕ)	Product distribution (%)								
		\underline{d}_0	\underline{d}_1	\underline{d}_2	\underline{d}_3	\underline{d}_4	\underline{d}_5	\underline{d}_6	\underline{d}_7	\underline{d}_8
Calculated A ^a	412	0.5	3.7	12.2	23.1	27.3	20.6	9.7	2.6	0.3
Expt. on alumina	416	0.2	0.5	3.0	16.6	40.3	38.4	1.0	-	-
" silica-alumina I	402	0.2	0.6	5.5	22.4	39.3	27.5	3.8	0.6	0.1
" silica-alumina II	402	0.1	0.5	4.4	21.0	41.7	31.3	0.9	0.1	-
Calculated B ^b	400 + 3	0.0	0.6	5.0	20.1	40.4	32.9	1.0	-	-

^a Distribution calculated for stepwise exchange assuming that all hydrogen atoms are exchanged the same rate. ^b Distribution calculated on the assumption that the molecules contain an average of 4.00 deuterium atoms in the ring positions and 0.03 in the side group for comparison with the experimental result on silica-alumina II.

ϕ value used. If multiple exchange is taking place or if the various hydrogen atoms are reacting at different rates the experimental distributions of products will only correspond to those calculated by the method above at conditions approaching equilibrium. Table 3.2 shows experimental distributions of isotopic benzenes at comparable stages of reaction on each of the three catalysts studied compared with the calculated distribution. The striking similarity between these distributions illustrate a number of points.

(a) the stepwise exchange character of these reactions since the distributions are taken at extents of reaction far from equilibrium ($\phi_{\infty} \simeq 570$). This provides useful confirmation of the validity of the conclusions drawn from the experimental values for $k\phi/k_0$.

(b) the relative unimportance of isotope effects in these exchange reactions. Thus for example the molecule $C_6H_3D_3$ on reaction will have an equal chance of replacing either a D or an H atom and similarly the difference between the rates of reaction of C_6H_6 and C_6D_6 are negligible.

(c) the validity of the assumptions used in the calculation of isotopic abundances from the mass spectrum of the compound and the accuracy obtained.

For molecules with two groups of hydrogen atoms reacting at different rates a more complicated procedure must be used to calculate distributions for comparison with those obtained

Table 3.2 A comparison of experimental and calculated product distributions for benzene exchange

Type	Extent of exchange (ϕ)	Product distribution (%)						
		d ₀	d ₁	d ₂	d ₃	d ₄	d ₅	d ₆
Expt. on silica-alumina I	233	5.4	20.0	31.7	26.6	12.7	3.3	0.4
" " silica-alumina II	230	5.5	20.3	31.8	26.6	12.5	3.1	0.2
" " alumina	230	5.6	20.5	31.8	26.7	12.0	3.1	0.3
Random *	230	5.5	20.5	31.9	26.4	12.3	3.1	0.3

* Distribution calculated for stepwise exchange assuming that all hydrogen atoms are exchanged at the same rate.

experimentally. In this case if both groups exchange by a stepwise mechanism ~~the~~ binomial distributions must be evaluated for each group using the appropriate value for ϕ in each case and then the two distributions are combined together.

Consider, for example, a molecule C_xH_n containing two groups of exchangeable hydrogen atoms (A) and (B), having a and b hydrogen atoms each. Then

$$a + b = n \quad (14)$$

If at any stage of reaction ϕ the extent of reaction of each group is given by ϕ_A and ϕ_B where

$$\phi = \phi_A + \phi_B \quad (15)$$

then by application of the binomial expansion (13) the distribution of isotopes in each group can be calculated for stepwise exchange. The contribution of these isotopes to any particular isotope di of the combined mass spectrum can then be calculated from the expression

$$di = \sum_{x=0}^{x=b} P_A(1-x) P_B(x) / 100 \quad (16)$$

where $P_A(1-x)$ is the percentage of isotope $d_{(1-x)}$ for group A and $P_B(x)$ is the percentage of isotope dx for group B.

The ϕ values for each group at any particular time can be calculated knowing the different rates of reaction for the two groups. Alternatively, the ϕ values can be chosen to give the best fit with the experimental results and then the difference in reaction rate between the two groups can be calculated. A sample calculation is given below for the case of toluene where

the ring hydrogen atoms exchange faster than those in the side group.

Take 100 molecules of hydrocarbon. Therefore there are 800 exchangeable hydrogen atoms. If at a particular time t , it is found that there are 400 D atoms in the ring position (ϕ_A) and 8 in the side group (ϕ_B), the total amount of deuterium in the hydrocarbon will be given by:

$$\phi = \phi_A + \phi_B = 408$$

If the rate of exchange of both groups of hydrocarbons were the same then at this extent of reaction ϕ_A would be $\frac{5}{8}$ 408 and correspondingly ϕ_B would be $\frac{3}{8}$ 408.

One can now calculate how the 400 deuterium atoms are distributed among the 100 molecules of hydrocarbon by the use of the binomial expansion(13)

$$(1/5 + 4/5)^5$$

Thus	% d ₀	=	100 x 1	(0.2) ⁵	(0.8) ⁰	=	0.03
	% d ₁	=	100 x 5	(0.2) ⁴	(0.8) ¹	=	0.64
	% d ₂	=	100 x 10	(0.2) ³	(0.8) ²	=	5.13
	% d ₃	=	100 x 10	(0.2) ²	(0.8) ³	=	20.50
	% d ₄	=	100 x 5	(0.2) ¹	(0.8) ⁴	=	41.00
	% d ₅	=	100 x 1	(0.2) ⁰	(0.8) ⁵	=	32.70

Similarly the distribution of the 8 atoms in the side group positions can be obtained from the expansion of

$$(\frac{292}{300} + \frac{8}{300})^3$$

giving 92.23, 7.56, 0.21 and 0.00 percent of d₀, d₁, d₂ and d₃

respectively.

If we now take the molecule as a whole and consider the resultant amount of the various masses.

$$\begin{aligned}
 \% \text{ Mass 92} &= 0.03 \times 92.23/100 = 0.03 \quad (d_0 \text{ in ring and } d_0 \text{ in s.g.}) \\
 \% \text{ Mass 93} &= 0.03 \times 7.56/100 \quad (d_0 \text{ in ring and } d_1 \text{ in s.g.}) \\
 &\quad + 0.64 \times 92.23/100 = 0.60 \quad (d_1 \text{ in ring and } d_0 \text{ in s.g.}) \\
 \% \text{ Mass 94} &= 0.03 \times 0.21/100 \quad (d_0 \text{ in ring and } d_2 \text{ in s.g.}) \\
 &\quad + 0.64 \times 7.56/100 = 4.8 \quad (d_1 \text{ in ring and } d_1 \text{ in s.g.}) \\
 &\quad + 5.13 \times 92.23/100 \quad (d_2 \text{ in ring and } d_0 \text{ in s.g.})
 \end{aligned}$$

etc.

These values should correspond to the experimental values obtained for the distribution of products at the same ϕ value if both groups exchange by a stepwise mechanism and the relative amounts of deuterium in the two groups have been correctly assessed. To show the magnitude of the effect of rate differences on the observed distribution of products, distributions of isotopic toluenes at comparable ϕ values with different weighting factors are given in Table 3.3.

Two calculated distributions are given in Table 3.1; A corresponds to the distribution derived from the expression (13) on the assumption that all 8 atoms were equally reactive and as shown, it differs markedly from the experimental distributions. On the other hand distribution B, based on two groups of atoms, is in excellent agreement with the results on silica-alumina II and equally good agreement was obtained with the experimental results on the other catalysts in a similar manner. Results

respectively.

If we now take the molecule as a whole and consider the resultant amount of the various masses.

$$\begin{aligned}
 \% \text{ Mass } 92 &= 0.03 \times 92.23/100 = 0.03 \quad (d_0 \text{ in ring and } d_0 \text{ in s.g.}) \\
 \% \text{ Mass } 93 &= 0.03 \times 7.56/100 \quad (d_0 \text{ in ring and } d_1 \text{ in s.g.}) \\
 &\quad + 0.64 \times 92.23/100 = 0.60 \quad (d_1 \text{ in ring and } d_0 \text{ in s.g.}) \\
 \% \text{ Mass } 94 &= 0.03 \times 0.21/100 \quad (d_0 \text{ in ring and } d_2 \text{ in s.g.}) \\
 &\quad + 0.64 \times 7.56/100 = 4.8 \quad (d_1 \text{ in ring and } d_1 \text{ in s.g.}) \\
 &\quad + 5.13 \times 92.23/100 \quad (d_2 \text{ in ring and } d_0 \text{ in s.g.})
 \end{aligned}$$

etc.

These values should correspond to the experimental values obtained for the distribution of products at the same ϕ value if both groups exchange by a stepwise mechanism and the relative amounts of deuterium in the two groups have been correctly assessed. To show the magnitude of the effect of rate differences on the observed distribution of products, distributions of isotopic toluenes at comparable ϕ values with different weighting factors are given in Table 3.3.

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Table 3.3 Calculated distributions for isotopic toluenes when the ring and side group hydrogens are reacting at different rates.

ϕ value for molecule	ϕ value for ring positions	ϕ value for side group positions	Product distribution (%)								
			d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
403	400	3	0.0	0.6	5.0	20.1	40.4	32.9	1.0	0.0	0.0
406	400	6	0.0	0.6	4.9	19.6	39.8	33.2	1.9	0.0	0.0
408	400	8	0.0	0.6	4.8	19.3	39.3	33.3	2.6	0.1	0.0
415	400	15	0.0	0.6	4.5	18.3	38.0	33.7	4.7	0.2	0.0
412	$5/8 \times 412^*$	$3/8 \times 412^*$	0.5	3.7	12.2	23.1	27.3	20.6	9.7	2.6	0.3

* equivalent to a random distribution where all hydrogens are equally reactive

for m-xylene are given in Table 3.4 and they confirm the evidence from the kinetic plots of Figure 3.4.

The distributions in Table 3.5 were obtained at earlier stages of reaction where side group exchange was negligible and before equilibrium conditions for exchange of the ring hydrogen atoms were obtained ($\phi_{\infty} \approx 490$ and 390 for toluene and m-xylene ring exchange respectively.) For each catalyst the experimental distributions correspond closely to random distributions calculated on the assumption that only ring hydrogen atoms were replaced. This agreement shows that all the ring hydrogens in each molecule are equally reactive in exchange. It should be noted that comparisons of this type must be made at ϕ values which are far from the equilibrium value otherwise random distributions will always be obtained irrespective of whether there are differences in reactivity or not.

3.3 Rates

Rates of reaction were determined by application of equations (1) and (2) in the case of benzene and equations (7) and (8) for the toluene and m-xylene side groups using $b = 3$ and 6 respectively. The rates of reaction of the toluene and m-xylene ring hydrogen atoms were obtained from equations (1) and (2) replacing ϕ by ϕ_A as determined by the expression (11). Typical ϕ plots are shown in Figures 3,5 for reactions on alumina. Similar straight lines were obtained from the corresponding d_o plots. These types of plots were obtained on all catalysts when the reaction was non poisoned.

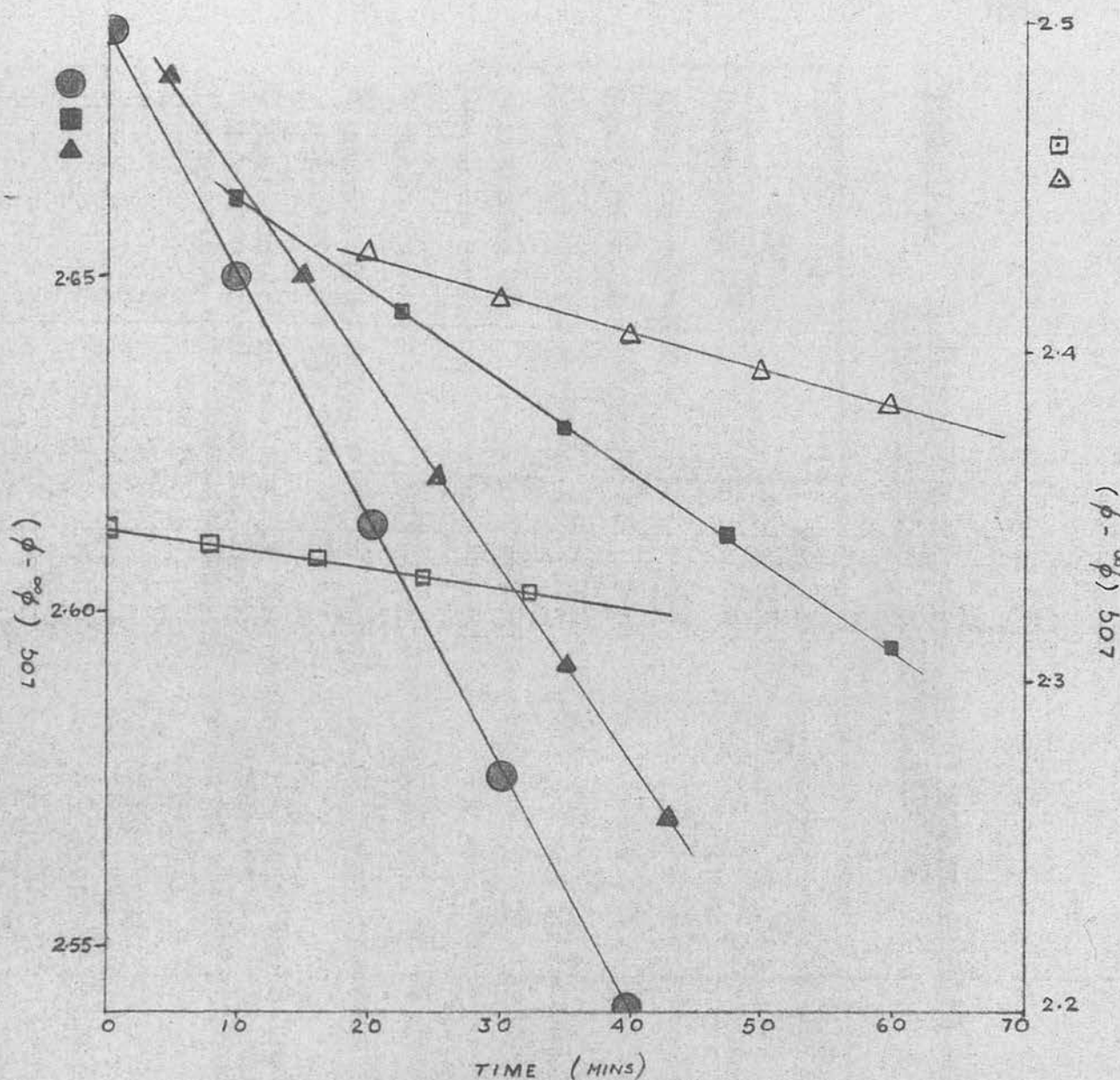


FIGURE 3.5

Plots for reactions on 0.08 gms. alumina.

- BENZENE AT 63°C.
- TOLUENE (RING HYDROGENS) AT 56°C.
- ▲ m-XYLENE (RING HYDROGENS) AT 93°C.
- TOLUENE (SIDE GROUP HYDROGENS) AT 267°C.
- △ m-XYLENE (SIDE GROUP HYDROGENS) AT 231°C.

Table 3.4. A comparison of experimental and calculated product distributions for m-xylene exchange

Type	Extent of exchange (ϕ)	Product distribution (%) ^a								
		d ₀	d ₁	d ₂	d ₃	d ₄	d ₅	d ₆	d ₇	d ₈
Calculated C ^b	280	3.7	14.6	25.5	26.4	18.0	8.4	2.7	0.6	0.1
Expt. on alumina	280	1.4	9.2	25.1	37.6	25.2	1.4	0.1	-	-
Expt. on silica-alumina II	280	1.4	8.9	26.1	37.9	23.1	2.5	0.1	-	-
Expt. on silica-alumina I	271	2.0	12.3	28.3	33.2	18.8	4.6	0.7	0.1	-
Calculated D ^c	24C + 30	1.9	11.9	29.1	33.9	18.6	4.1	0.5	-	-

^a There were negligible amounts of products with 9 or 10 deuterium atoms.

^b Distribution calculated for step-wise exchange assuming that all hydrogen atoms are exchanged at the same rate.

^c Distribution calculated on the assumption that the molecules contain an average of 2.40 deuterium atoms in the ring positions and 0.30 in the side groups for comparison with the experimental result on silica-alumina I.

Table 3.5. Distributions to show the equivalence of the ring hydrogen atoms in the exchange reactions

Hydrocarbon	Catalyst	Extent of exchange (ϕ)	Product distribution (%)					
			d_0	d_1	d_2	d_3	d_4	d_5
Toluene	Silica-alumina I	261	2.4	13.5	30.2	32.3	17.5	4.1
	Silica-alumina II	262	2.3	13.1	30.4	32.7	17.5	4.0
	Alumina	262	2.5	13.0	30.3	33.0	17.1	4.1
	Calculated \bar{r}^a	263	2.4	13.2	29.4	32.8	18.2	4.0
m-xylene	Silica-alumina I	151	15.5	36.2	32.8	13.2	2.3	-
	Silica-alumina II	151	15.4	36.0	33.2	13.3	2.1	-
	Alumina	150	15.2	37.2	32.1	13.4	2.1	-
	Calculated \bar{r}^b	150	15.3	36.6	32.9	13.2	2.0	-

^a Random distribution assuming 5 equally exchangeable hydrogen atoms.

^b Random distribution assuming 4 equally exchangeable hydrogen atoms.

In order to compare the rates of exchange of the hydrocarbons a series of four runs was carried out using the same catalyst sample. Each series involved the exchange of benzene, toluene, *m*-xylene and finally benzene again with reactivation of the catalyst between each run. The validity of this procedure was tested using a sample of silica-alumina I and carrying out a number of consecutive benzene exchange reactions on one sample. The results, illustrated in Figure 3.6, show that the catalyst activity could be reproduced if the activation procedure was kept standardised. However, if the temperature of activation and outgassing is raised a change in activity is produced which is not reversible under the conditions of these experiments. Thus if valid comparisons are to be made between the exchange rates of the various hydrocarbons, the activation procedure must be kept constant and in no case should the temperature of this treatment be raised above that for the previous run.

The results in Figure 3.7 for alumina show the maximum decrease in activity between the initial and final runs with benzene observed with any sample. With silica alumina I the relative rates of the four runs for the exchange of the aromatic ring hydrogen atoms were 1:0.5:0.4:0.8 and for silica-alumina II the ratios were 1:1.6:0.8:6.3. Repeat experiments with toluene and *m*-xylene on fresh samples of the two silica-alumina catalysts gave rates close to those for the initial runs with benzene. A second series on a fresh sample of alumina showed a maximum spread by a factor of 1.6 between any two runs with all the rates

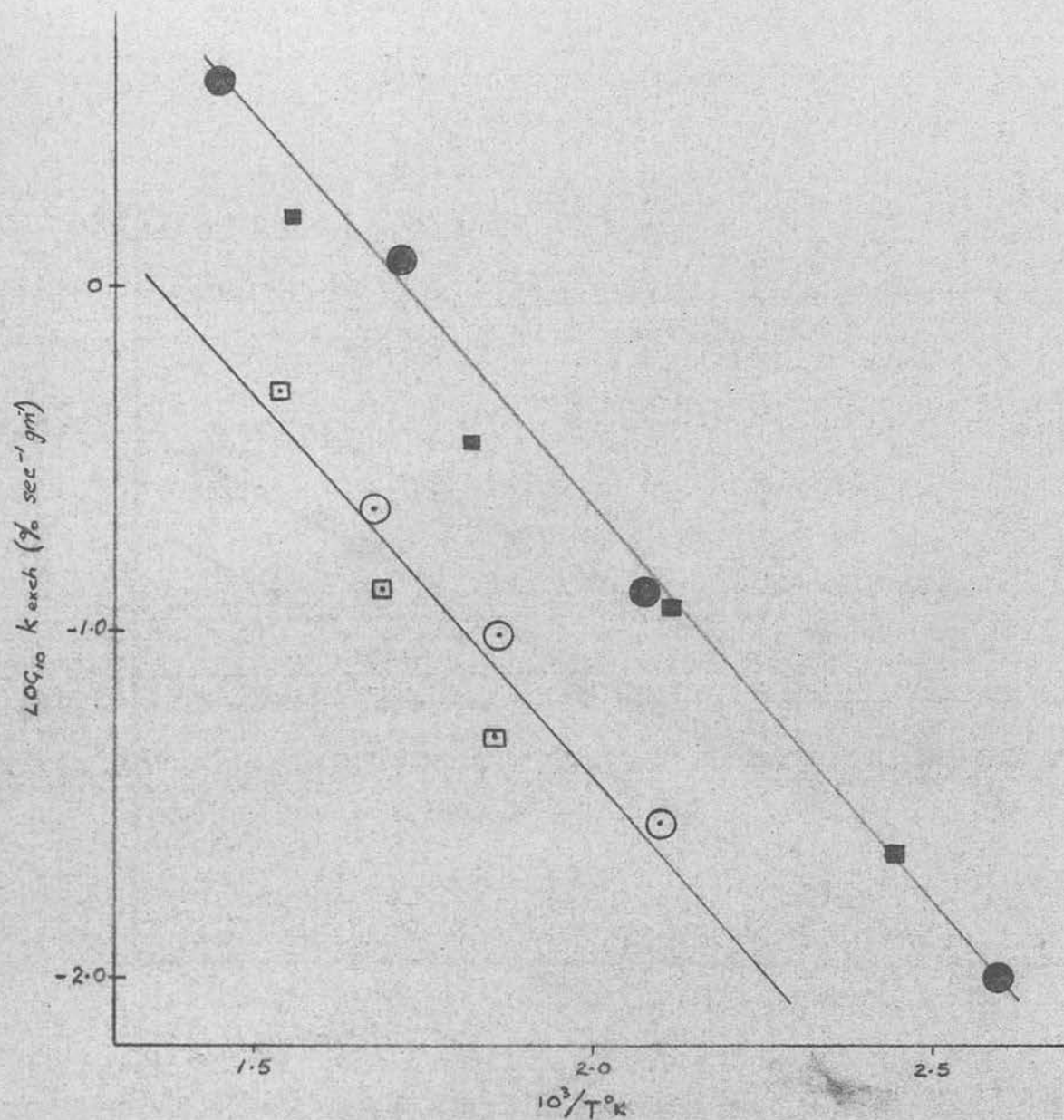


FIGURE 3.6

ARRHENIUS PLOTS FOR BENZENE EXCHANGE ON ONE SAMPLE OF SILICA
ALUMINA I

- RUN 1 ACTIVATED AND OUTGASSED AT 520°C
- RUN 2 " " " " 520°C
- RUN 3 " " " " 660°C TWICE
- RUN 4 " " " " 520°C

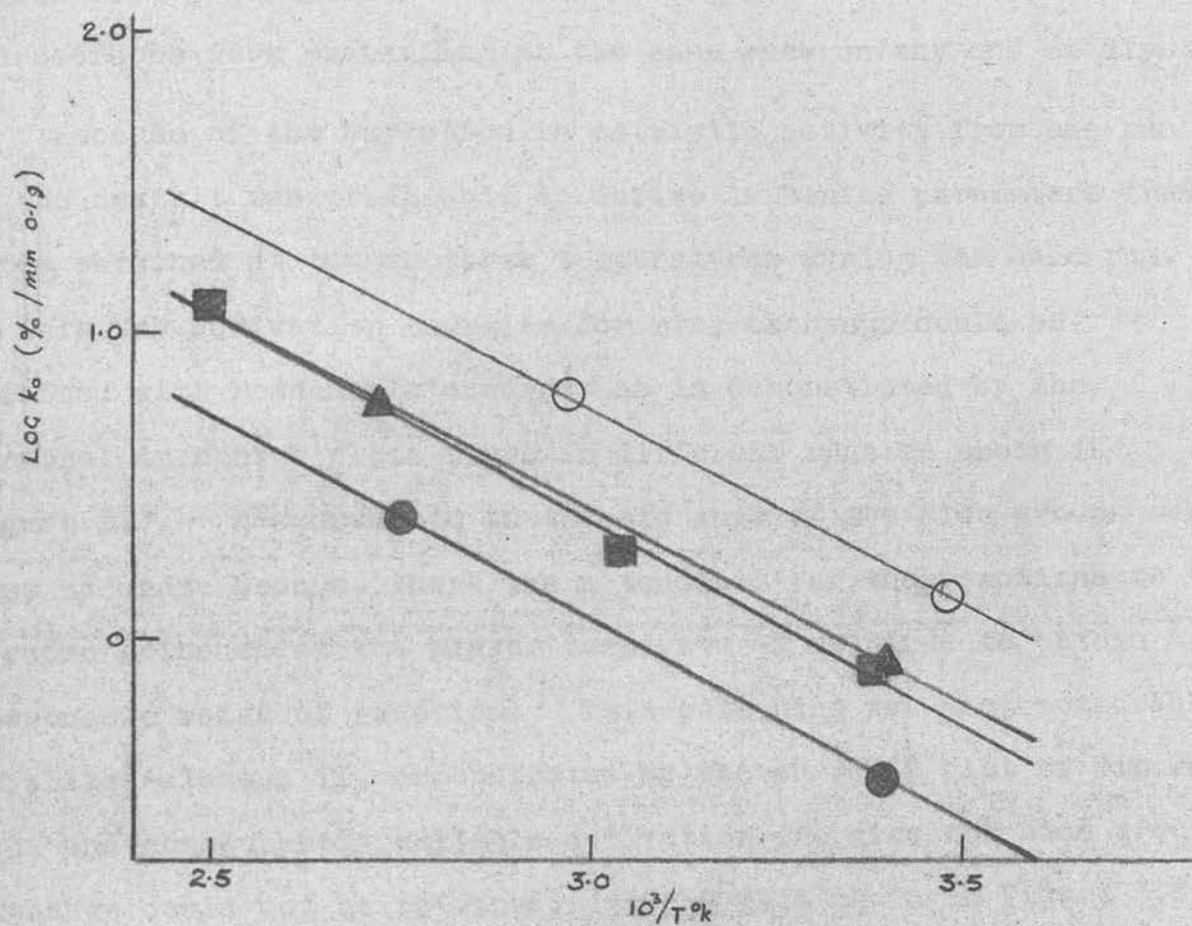


FIGURE 3-7

ARRHENIUS PLOTS FOR A SERIES OF EXCHANGE RUNS ON A SAMPLE OF γ -ALUMINA IN THE SEQUENCE BENZENE ○, TOLUENE ■, m -XYLENE ▲ AND BENZENE ●. PLOTS FOR TOLUENE AND m -XYLENE ARE FOR REACTION OF THE HYDROGEN ATOMS IN THE RING POSITIONS.

falling between those for the initial and final runs for benzene shown in Figure 3.7. These results showed that within the limits of reproducibility the ring hydrogen atoms in all three hydrocarbons were exchanging at the same rate on any one catalyst.

Because of the variation in catalytic activity from one run to the next it was preferable to derive Arrhenius parameters from rates obtained at two or three temperatures during the same run. In this way activation energies for ring exchange could be obtained with reasonable accuracy as is demonstrated by the parallel Arrhenius plots found in different runs as shown in Figure 3.7. Measurements on the exchange of the side groups were less accurate because there was a tendency for the reactions to become poisoned at the higher temperatures required to obtain reasonable rates of reaction. This poisoning was most noticeable on silica-alumina II, demonstrated by the curved ϕ plot of Figure 3.8, and consequently reliable activation energies for side group exchange could not be obtained. The ϕ plot shown in Figure 3.8 is for benzene exchange. Consequently the curvature cannot be due to differences in reactivity of the various hydrogen atoms and thus must be attributed to a poisoning process. However, no loss of hydrocarbon from the gas phase was detected even when poisoning was occurring. The poisoning on the other two catalysts was usually less severe and reasonably accurate measurements of Arrhenius parameters were possible. The type of Arrhenius plots obtained for unpoisoned runs is demonstrated in Figure 3.9 for the exchange of the ring and side group hydrogen atoms in

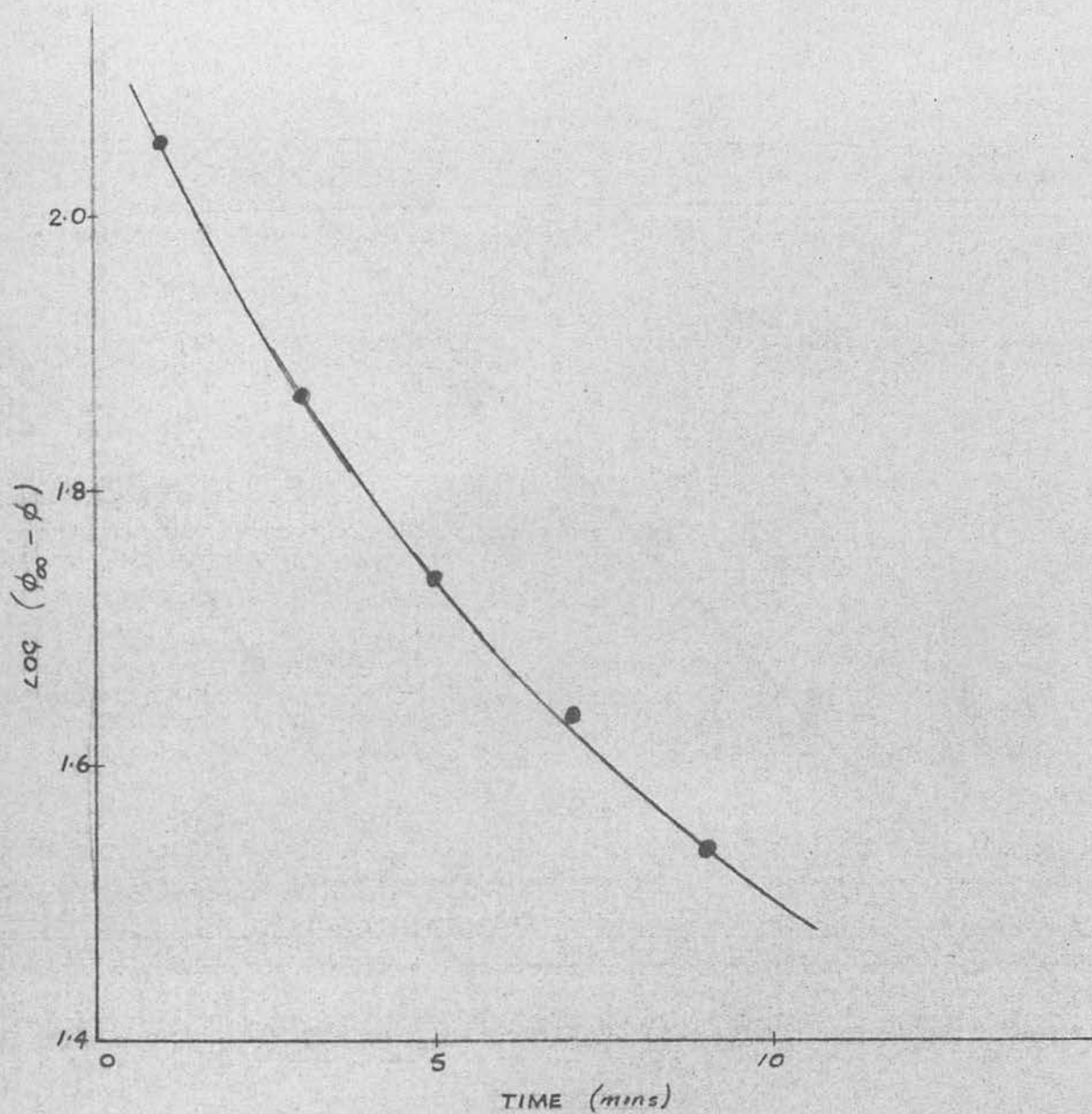


FIGURE 3.8

CURVED ϕ PLOT FOR EXCHANGE OF BENZENE ON
SILICA-ALUMINA II AT 129°C DUE TO
POISONING OF CATALYST ACTIVITY.

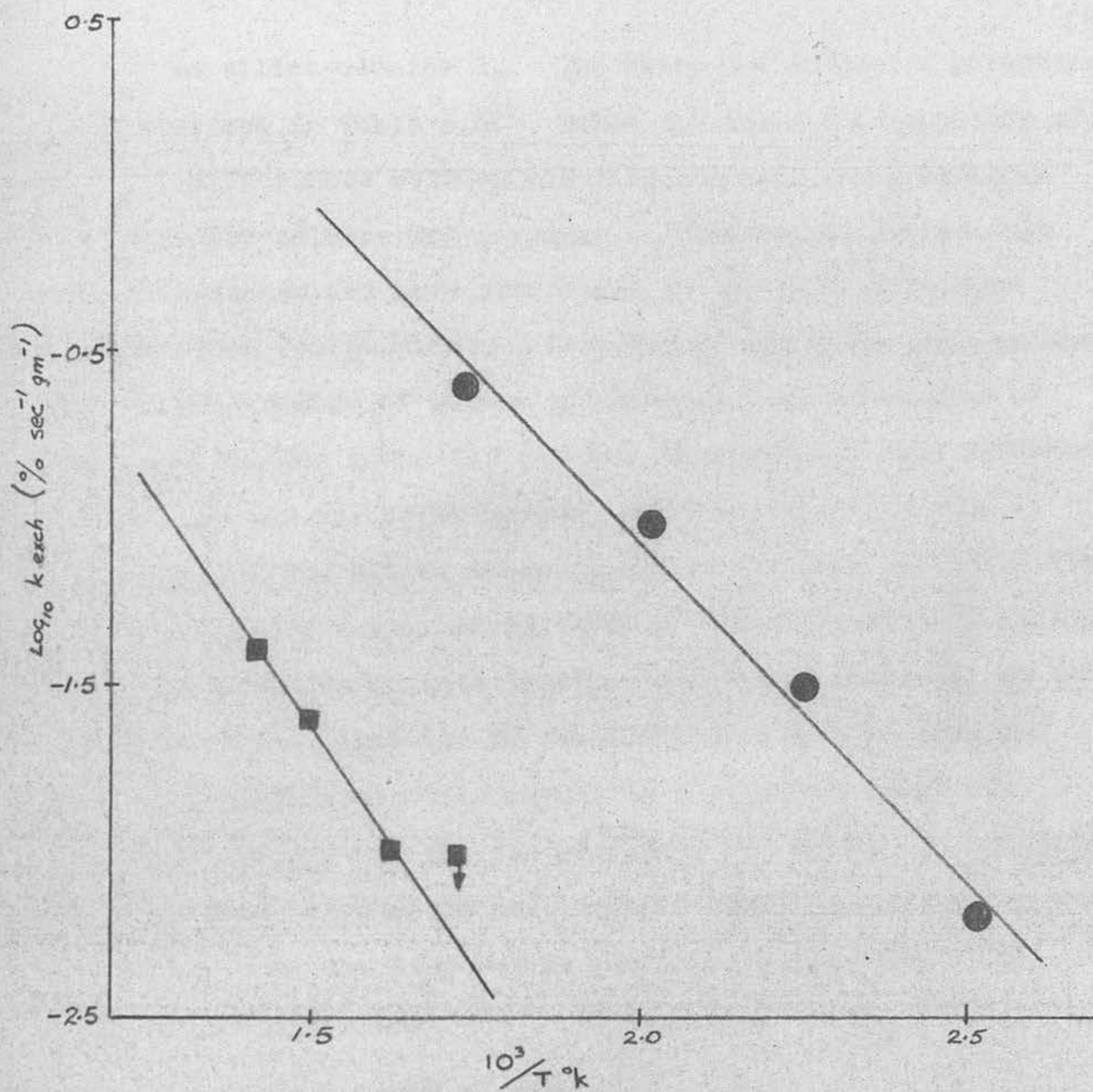


FIGURE 3.9

ARRHENIUS PLOT FOR THE EXCHANGE OF TOLUENE ON
SILICA - ALUMINA I.

- EXCHANGE OF RING HYDROGEN ATOMS.
- EXCHANGE OF SIDE GROUP HYDROGEN ATOMS.

toluene on silica-alumina I. The rates and Arrhenius parameters are summarised in Table 3.6. Table 3.7 shows the magnitude of the rate differences between the ring and side group exchange reactions for toluene and *m*-xylene. Considering groups, the rate differences are more pronounced in the case of toluene exchange than for *m*-xylene. However, if one takes into account the relative number of places of exchange i.e. the number of hydrogens in each group for the two molecules, the rate differences between the two molecules become very similar at the same temperature. The slight disagreement in the case of silica-alumina II can easily be explained in terms of the difficulty of making these measurements on this catalyst due to the poisoning of the reaction. The magnitude of the difference between ring and side group reactivity will depend on temperature since the activation energy for the two processes are different, but, since the same effects apply to both toluene and *m*-xylene and are of the same magnitude, the temperature chosen will not affect the comparisons made here.

3.4 Specially treated alumina

The exchange of toluene was followed on alumina which had been subjected to two different pretreatments consisting of

(a) after normal pretreatment, exposure to oxygen at 100 torr for 30 min. at 520°C, cooling to 20°C and evacuating for 1 hr. and

(b) after normal pretreatment exposure to deuterium at 45 torr for 1 hr. at 520°C, and after evacuation for 10 min., exposure to a further dose of deuterium at 18 torr for 1 hr.

Table 3.6. Rates and Arrhenius Parameters for exchange.

Catalyst	Exchange reaction	Temp range (°C)	E (kcal/mole)	log ₁₀ A (A in mol/sec cm ²)	Temp (°C) for k=1%/min, 0.1
Silica-alumina I	benzene	125 to 330	10.2 ± 1.0	14.2 ± 0.6	212
	toluene, ring	125 to 330	10.0 ± 1.0	13.6 ± 0.6	258
	toluene, side group	300 to 440	13.8 ± 1.0	13.5 ± 0.6	547
	m-xylene, ring	125 to 330	11.1 ± 1.0	14.3 ± 0.6	232
	m-xylene, side group	300 to 440	13.4 ± 1.0	13.6 ± 0.6	441
Silica-alumina II	benzene	20 to 100	6.9 ± 1.0	15.7 ± 0.6	-5
	toluene, ring	20 to 100	7.6 ± 1.0	15.9 ± 0.6	16
	toluene, side group	0.06%/min	0.1g at 100°C		
	m-xylene, ring	20 to 100	6.6 ± 1.0	15.8 ± 0.6	8
	m-xylene, side group	0.6%/min	0.1g at 100°C		
Alumina	benzene	20 to 130	6.0 ± 0.5	14.0 ± 0.3	27
	toluene, ring	20 to 130	6.1 ± 0.5	14.1 ± 0.3	31
	toluene, side group	150 to 250	12.3 ± 1.0	15.3 ± 0.6	205
	m-xylene, ring	20 to 130	6.0 ± 0.5	14.0 ± 0.3	27
	m-xylene, side group	150 to 250	11.9 ± 1.0	15.4 ± 0.6	172

* Rates expressed as %/min 0.1g are convenient for comparing catalyst activities.

Table 3.7 Comparison between ring and side group hydrogen exchange rates for toluene and m-xylene

Catalyst	Temp. °C	Rates			
		Ring exchange/Side group exch.		Ring exch./Side group exch. $\times \frac{n^1}{n}$	
		toluene	m-xylene	toluene	m-xylene
silica-alumina I	300	81	29	48.5	43.5
silica-alumina II	100	282	72	170	108
alumina	150	89	32	53.5	48.0

*
n = no of hydrogens in ring positions
n¹ = no of hydrogens in side group positions

followed by evacuation for 1 hr. at 520°C.

The results are presented in Figures 3.10 and 3.11. These runs were carried out on the same sample of catalyst and the activity was checked before and after the runs by carrying out exchange reactions with toluene after the normal activation procedure. Figure 3.10 shows that the normal rate of exchange was found after pretreatment (b) but after pretreatment (a) the rate was slower by a factor of 6 at 22°C. Figure 3.11 shows the rate of the exchange reaction after pretreatment (b), from the time the gas mixture was admitted to the catalyst. From the graph it can be seen that good straight line plots were obtained and there was no evidence of any appreciable initial burst of reaction. In fact the initial reaction seems to be of an acceleratory nature, but the effect is very small.

3.5 Isomerisation of m-xylene

Some experiments were carried out to determine the rates of isomerisation of m-xylene under similar conditions to those used for the exchange reaction. After reaction for a known time at a fixed temperature the hydrocarbon was frozen into a sample tube, diluted with pentane and analysed by gas-liquid chromatography as described previously. It was found that most samples of reacted m-xylene contained small amounts of benzene or toluene. However, these were not taken to be reaction products, since blank samples of m-xylene (i.e. samples obtained in the usual manner but without the catalyst in the reaction vessel) also showed the presence of these compounds. The impurities

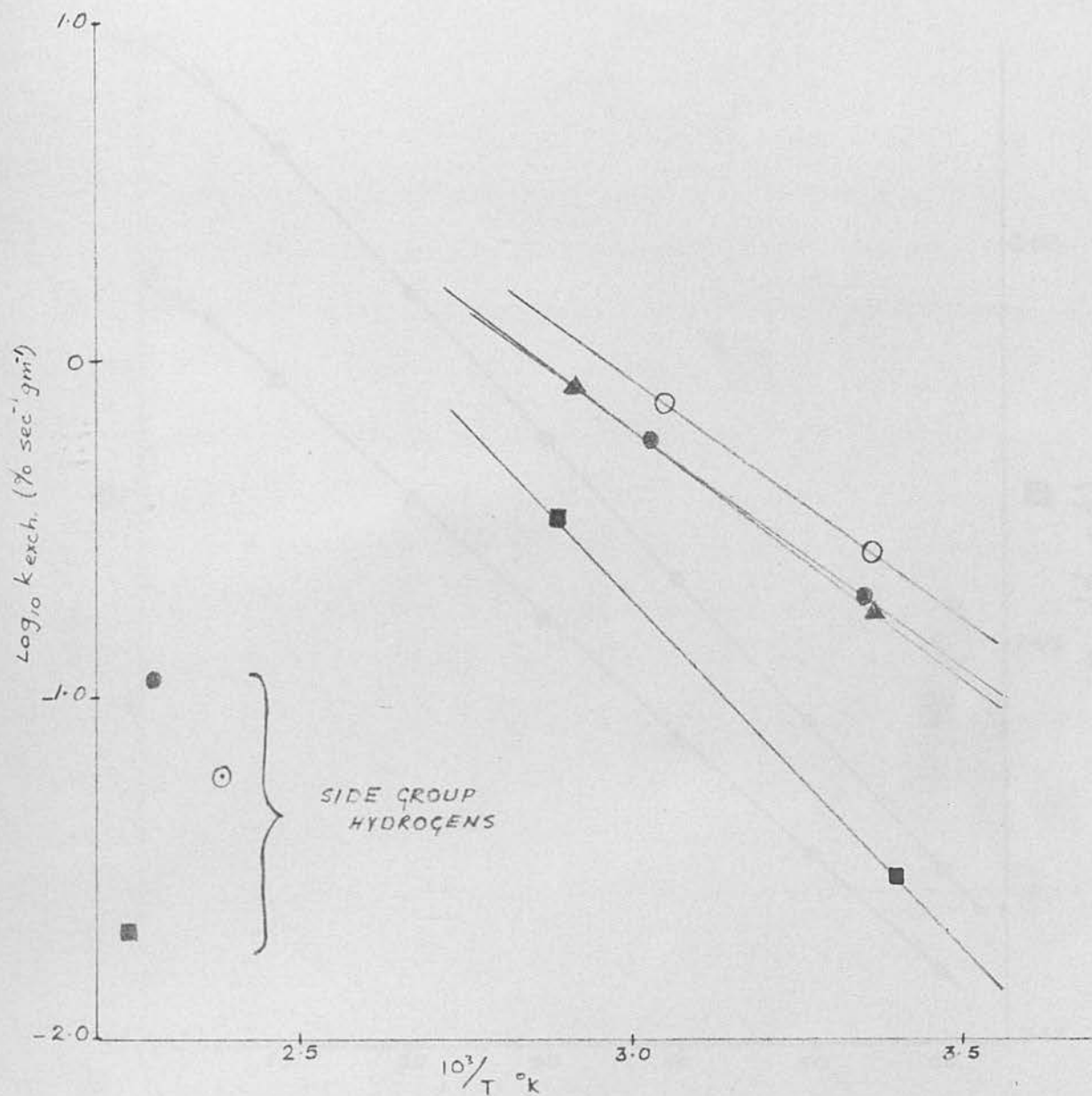


FIGURE 3-10

ARRHENIUS PLOTS FOR EXCHANGE OF TOLUENE ON SPECIALLY TREATED ALUMINA.

- RUN 1 NORMAL PRETREATMENT.
- RUN 2 PRETREATMENT (a)
- ▲ RUN 3 PRETREATMENT (b)
- RUN 4 PRETREATMENT NORMAL

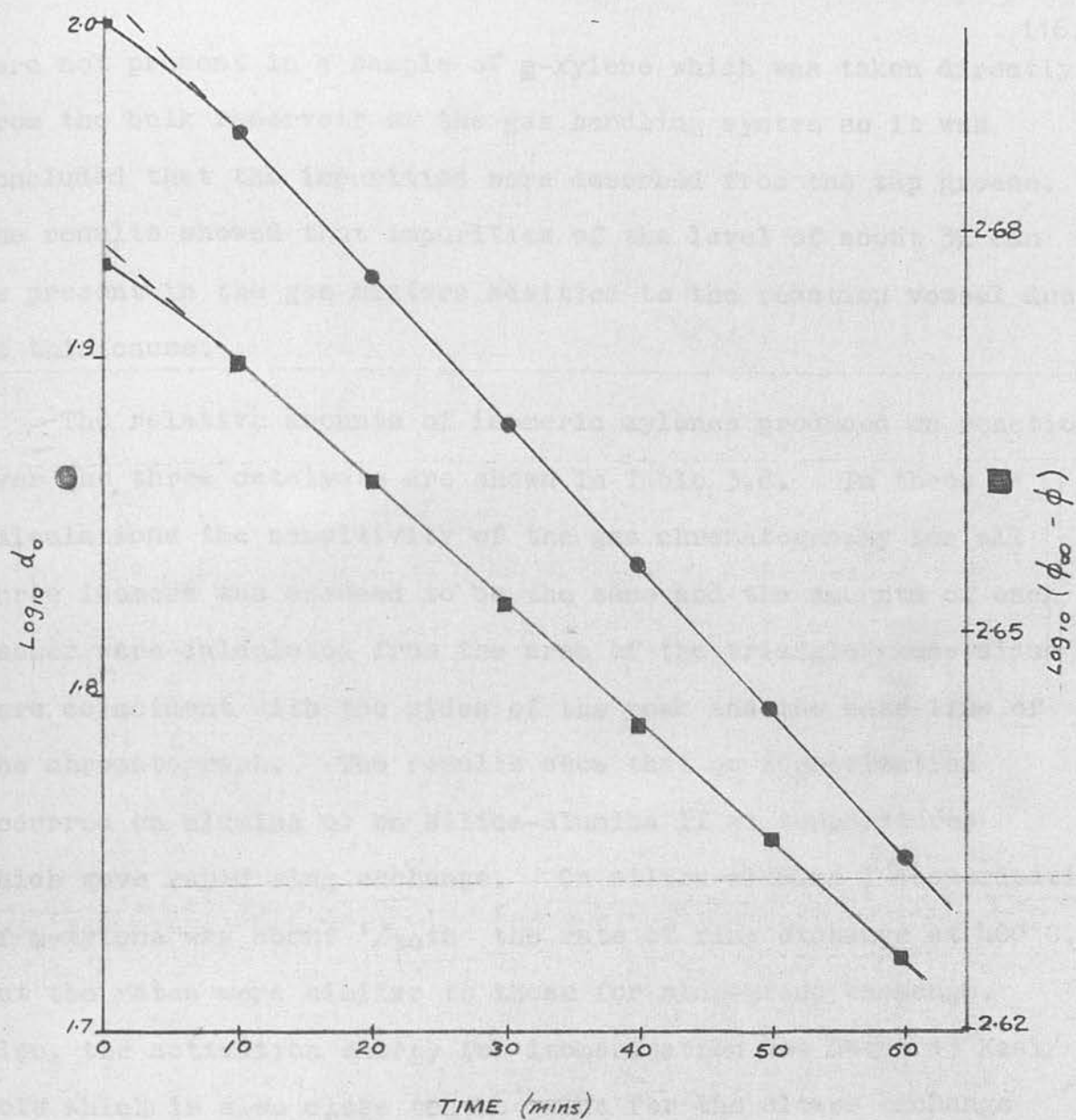


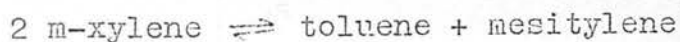
FIGURE 3.11

RATE PLOTS FOR EXCHANGE OF TOLUENE AT 25°C ON
ALUMINA AFTER PRETREATMENT (b)

were not present in a sample of *m*-xylene which was taken directly from the bulk reservoir on the gas handling system so it was concluded that the impurities were desorbed from the tap grease. The results showed that impurities of the level of about 3% can be present in the gas mixture admitted to the reaction vessel due to this cause.

The relative amounts of isomeric xylenes produced on reaction over the three catalysts are shown in Table 3.8. In these calculations the sensitivity of the gas chromatography for all three isomers was assumed to be the same and the amounts of each isomer were calculated from the area of the triangle whose sides were coincident with the sides of the peak and the base line of the chromatograph. The results show that no isomerisation occurred on alumina or on silica-alumina II at temperatures which gave rapid ring exchange. On silica-alumina I isomerisation of *m*-xylene was about $1/30$ th the rate of ring exchange at 400°C, but the rates were similar to those for side-group exchange. Also, the activation energy for isomerisation was about 13 Kcal/mole which is also close to the value for the slower exchange process.

As well as isomerisation there is a possibility that the *m*-xylene will disproportionate



Only the sample obtained after reaction for 33 mins. at 435°C showed any trace of mesitylene and thus it was assumed that this

Table 3.8. Isomerisation of *m*-xylene

Catalyst	reaction time (min)	Reaction temp. (°C)	Composition of xylenes (%)			Initial rate (%/min 0.1g)
			<i>o</i>	<i>m</i>	<i>p</i>	
Silica-alumina I	64	202	-	100	-	-
Silica-alumina I	33	310	2	96	2	0.03
Silica-alumina I	33	390	11	77	12	0.23
Silica-alumina I	33	435 ^a	13	73	14	0.29
Silica-alumina II	30	98	-	100	-	-
Alumina	30	236	-	100	-	-
Calculated for equilibrium		427	24.4	52.1	23.5	-

^a Some mesitylene detected.

reaction was unimportant in the temperature ranges studied. Although toluene is also produced in this reaction it was decided unwise to estimate the amount of disproportionation by the relative amounts of toluene and xylene since the toluene may be an impurity and not a reaction product. Any trace of mesitylene, however, must come from reacted xylene since the gas handling system was free from this impurity. Errors arising from the analysis of reacted *m*-xylene will tend to lower the extent of reaction since there may be more *m*-xylene in the sample taken for analysis than there was originally in the reaction vessel, due to desorption of unreacted *m*-xylene from the tap grease.

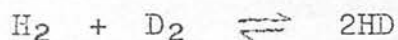
3.6 Hydrogen/Deuterium Exchange

Hydrogen/deuterium exchange reactions were carried out on the three catalysts using equal pressures (13 torr) of hydrogen and deuterium. For each catalyst the activation and evacuation procedure was the same as that used for the exchange experiments but was carried out at a lower temperature (450°C). Temperatures higher than this could not be used since the furnace used to heat the catalyst was made from an aluminium block which tended to melt at temperatures around 500°C. Analysis of the exchange reaction was effected by an MS 10 mass spectrometer attached to the reaction vessel via a fine capillary leak and the change in the relative amounts of D_2 , HD and H_2 were measured by the relative peak heights at masses 4, 3 and 2. The method of calculation of rates from these data is discussed in Part II of this

thesis.

Rapid exchange occurred at -93°C on both silica-alumina II and alumina, the latter showing a slow reaction ($0.05\%/ \text{min } 0.1\text{g}$) even at liquid nitrogen temperature (Figure 3.12.). In contrast higher temperatures were required for silica-alumina I which gave rates of 0.6 and $2.8\%/ \text{min } 0.1\text{g}$ respectively, at 153°C and 199°C . These values correspond to an activation energy of 13 Kcal/mole and a frequency factor expressed as $\log_{10}A$ (A in mol/sec cm^2) of 17.1.

The hydrogen deuterium exchange reaction



is faster on all three catalyst than the corresponding exchange reactions of benzene, toluene and m-xylene, although the rate differences are more pronounced in the case of silica-alumina II and alumina than on silica-alumina I.

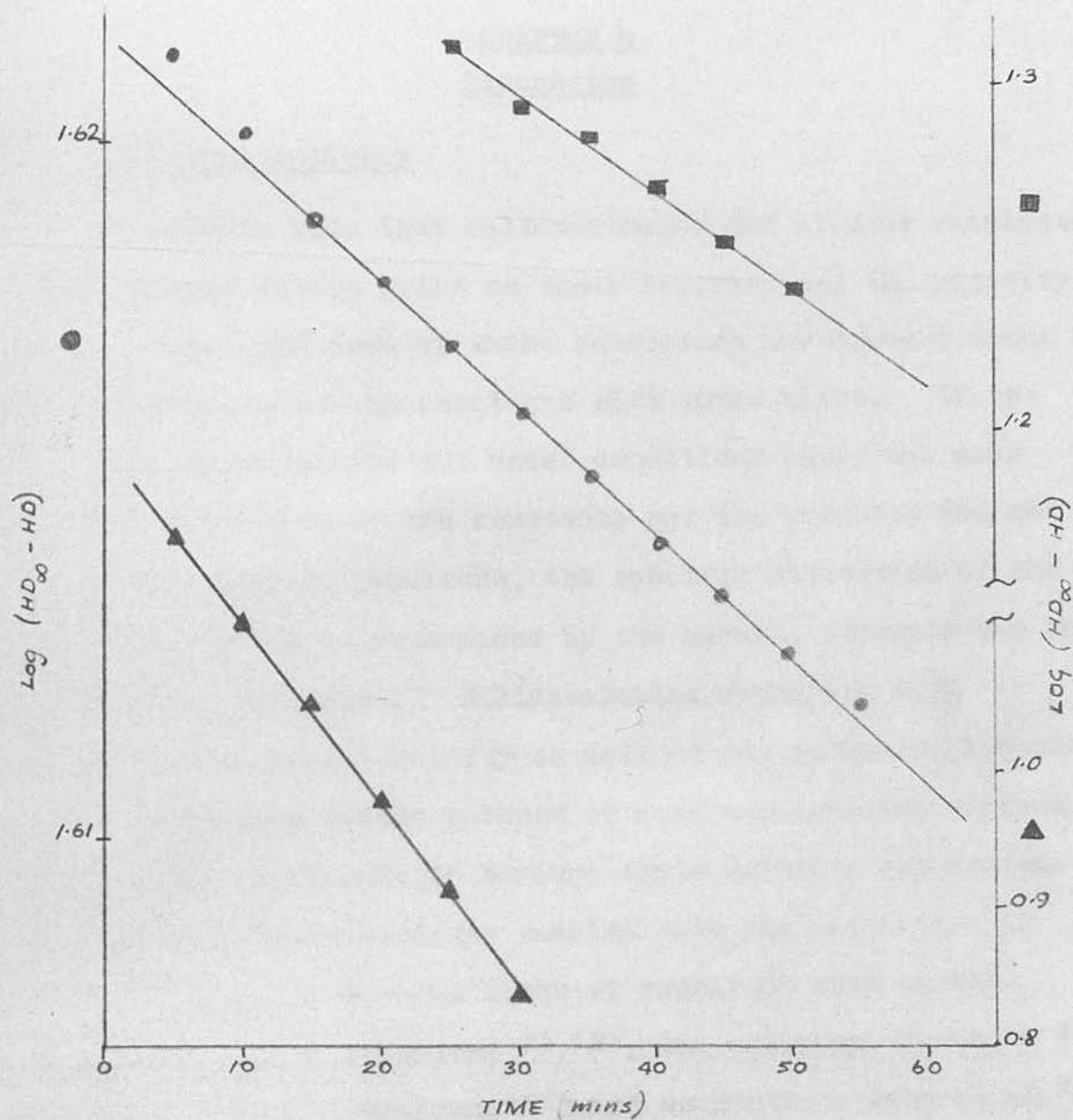


FIGURE 3-12

RATE PLOTS FOR THE REACTION $H_2 + D_2 \rightleftharpoons 2HD$

- ALUMINA AT LIQUID NITROGEN TEMPERATURE -195°C .
- SILICA ALUMINA I AT 153°C
- ▲ " " " 199°C

CHAPTER 4

Discussion

4.1 Catalytic Activity

It is well known that silica-alumina and alumina catalysts possess strong acidic sites on their surfaces and the majority of reactions catalysed by these substances are brought about by the interaction of the reactants with these sites. If the reactions were carried out under conditions where the mass transfer processes of the reactants and the products did not affect the rate of reactions, the specific activities of the catalysts should be determined by the amount, strength and the type of the acid site. Silica-alumina catalysts show γ of non-protonic (Lewis) acidity as well as the protonic (Brönsted) one. Each type covers a range of acid strengths and various attempts have been made to measure their relative abundances. Some authors correlated the results with the activities of the catalysts for several kinds of reactions such as the polymerisation of propylene ^{24,124}, the cracking of cumene ^{24,125} hydrogen transfer reactions ¹²⁴ and so forth. Sato et al. ²⁹ have made similar measurements on a variety of silica-alumina catalysts with varying amounts of alumina. Comparisons of this type are, however, difficult to make for a number of reasons. The catalyst nature may change on contact with reactants, especially if water is present, and so acidity measurements should ideally be made under reaction conditions. The acid sites present on one

catalyst vary in strength and depending on the reaction studied only a certain range of these sites may be important. Thus if the distribution of acidic strength varies over the range of catalysts the activity may also vary although the total measured number of sites may be similar. The results of Sato et al suggest that protonic acid sites seem to be responsible for the polymerisation of olefins, the cracking of cumene and the disproportionation of toluene while non protonic ones are active for the decomposition of isobutane. They also suggested that the effectiveness of the protonic sites does not change in the case of the polymerisation, but in the cracking and disproportionation reactions they change with the composition of the catalyst.

The results presented here show that at 100°C silica-alumina II is 10 times more active than alumina and 1000 times more active than silica-alumina I for exchange of the ring hydrogen atoms in benzene, toluene and m-xylene. There is no correlation between these exchange reactions and the activity pattern for cumene cracking. The latter reaction is most favoured on catalysts similar in composition to silica-alumina I, and thus it appears that the strongly acidic sites, mainly protonic in nature, which are present on such silica-aluminas are not essential for the exchange processes reported here. The activity of alumina which in the dehydrated form used here has been shown by many workers to be a Lewis acid type catalyst confirms this view.

The variations in catalyst activity which were observed

over the series of runs may be associated with minor differences in the pretreatment of the catalysts which may include some variation in the amount of water retained on the surface. Hindin and Weller ¹⁰⁵ have shown that both activation temperature and water content influence the activity of alumina for the exchange of hydrogen and deuterium, and for the hydrogenation of ethylene. For both reactions they found that the catalytic activity increased with drying time and temperature. Water was found to be a catalyst poison, the reaction being inhibited by coverage of as little as 2% of the available surface. The poisoning by water was dependent on the temperature at which it was added to the catalyst, and the increase in activity caused by removal of a given amount of water was lost by addition to the dried catalyst of a smaller amount.

On silica-alumina Hindin, Mills and Oblad ¹²⁶ found that the exchange of isobutane on a deuterated catalyst was also dependent on water content. They found, however, that the catalytic activity decreased as the drying temperature was increased from 200 to 525°C. Back addition of very small amounts of water (0.2% of catalyst weight) to a catalyst dried at 525°C produced a large increase in activity which rapidly fell off as the amount of water was increased. Similar results were also reported by Hansford ⁷⁰. Danforth ⁶⁷ explains these effects by the movement of water as a co-catalyst from site to site which may function to displace the hydrocarbon from its catalyst

complex or introduce D from D_2O into the hydrocarbon with formation of a carbonium ion. The active site is considered to be a Lewis acid and the poisoning effect of excess water corresponds to the complete hydration of these sites. A maximum in activity should thus occur when about half of the sites are covered by D_2O .

Small traces of other substances may also contribute to the variations in activity reported here. Hansford ⁷⁰ reports that the exchange of isobutane with D_2O on silica-alumina is favoured by the addition of small amounts of isobutene which easily forms a carbonium ion by addition of a proton and initiates the exchange reaction by abstraction of a hydride ion. Larson and Hall ¹²⁷ have shown that carbon dioxide poisons the exchange of methane and deuterium on alumina. In addition to these the rate of reaction may be lowered by trace amounts of other poisons such as sulphur compounds and bases which are strongly adsorbed on the catalyst surface.

In view of these facts it seems most likely that the variations in activity observed in the present work were due to the presence of small traces of impurities in the gas mixture. Although there may have been minor differences in the activation conditions they are too small to account for the differences obtained and the result of Figure 3.6 for silica-alumina I show that at least for this catalyst the changes in activity with different outgassing temperatures are not reversible under the

conditions studied. Reversible conditions may be obtained if the catalyst was rewetted after each run, but in the work reported here this was not the case. As demonstrated by the gas chromatographic results appreciable amounts of impurities can be desorbed from the tap grease during the preparation of a gas mixture and these impurities may have led to the observed differences in activities. On several occasions during exchange experiments on alumina inactive catalysts were produced. On such runs temperatures of the order of 300°C were required to produce the same activity as that which would have occurred at room temperature for a normal run. The failure of the catalyst to bring about the exchange reaction was attributed to the presence of acetone impurities in the gas mixture since at the time when these phenomena occurred the dual purpose gas handling system had also been used to prepare acetone mixtures for reactions on TiO_2 ¹²⁸.

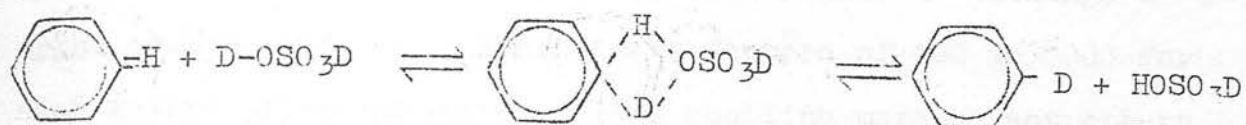
Apart from poisons inadvertently introduced to the catalyst by desorption from tap grease, a number of runs were seen to be poisoning during the exchange process. This was believed to be due to coke formation on the catalyst since after such runs the catalyst colour was dark brown. The severe poisoning on silica-alumina II at higher temperatures was attributed to its low surface area and high activity.

4.2 Comparison with Homogeneous Acid Catalysis

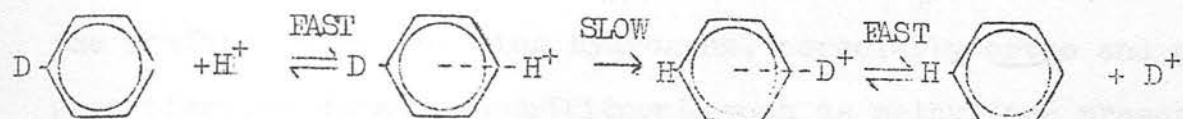
Many of the reactions catalysed by silica-alumina

catalysts are also catalysed by strong acids such as aluminium chloride or sulphuric acid. The nature of reactions like alkylation, skeletal isomerisation, polymerisation and isotopic exchange carried out on both silica-alumina and in sulphuric acid media show remarkable resemblance to one another. Burwell, Porte and Hamilton ¹²⁹ showed that the reactions of +3 methyl hexane with D_2O on silica alumina were markedly similar to those carried out in sulphuric acid and thus suggested that a similar mechanism was operating. This involved the formation of a carbonium ion with subsequent exchange and isomerisation; the hydrocarbon was regenerated by a hydride transfer mechanism. The reaction products over silica-alumina were deeply exchanged but the perdeutero hydrocarbon was formed to a negligible extent, as a results of the hydride transfer. Hansford et al ¹³⁰ observed similar trends in the exchange of isobutane with heavy water on silica-alumina. Initial products contained large amounts of the d_7 d_8 and d_9 isotopes, but only small amounts of the d_{10} isotope were found. They also report that traces of isobutylene accelerate the rate of exchange of isobutane. Similar effects have also been reported for reaction in sulphuric acid media ¹³¹.

The mechanism of exchange of aromatic molecules in acidic solution has been regarded by Ingold ¹³² as electrophilic substitution by attack at a single carbon atom, as in ordinary aromatic substitution.



Gold and Satchell ¹³³ proposed a mechanism of exchange of deuterated aromatics and H_2SO_4 in which the slow stage is the conversion of a π -type complex, with a proton and the aromatic nucleus in facile equilibrium with the solvent, to a π -type complex with the proton in the ring and the deuterium loosely bound.



Mackor, Smit and Van der Waals ¹³⁴ studied the rate of dedeuteration of deuterated benzene and a number of its alkyl substituted derivatives in a homogeneous system using $\text{CF}_3\text{COOH} + \text{H}_2\text{SO}_4$ mixtures as solvent and catalyst. A linear relationship was found between the logarithms of the first order rate constants and the Hammett acidity function for the $\text{CF}_3\text{COOH}/\text{H}_2\text{SO}_4$ mixture, and between the hydrocarbon basicity constants measured in anhydrous HF and its rate of deuteration. The relative rate constants for exchange of the hydrocarbons studied is given in Table 4.1.

Table 4.1 Rate constants (K) for dedeuteration of mono-D-methylbenzenes in CF_3COOH at 25°C , relative to p-xylene

Hydro-carbon	Ben-zene	o-Toluene	m-Toluene	p-toluene	p-xylene	4-m-xylene	mesitylene
log K	-3.1	-0.7	-2.6	-0.6	0.0	2.3	4.4

For these series of hydrocarbons the rate of exchange of the ortho or para hydrogens increases by factors of 100 to 1000 for each methyl group substituted in a position meta to any others present, and even the meta hydrogen of toluene is more active than in benzene. The order of reactivity of the compounds is typical for an electrophilic substitution reaction. In these reactions protons are the electrophiles and electronic rather than steric effects exert the predominating influence and are responsible for the activation of the ring hydrogens, especially ortho and para, when electron donating substituents such as methyl are present as side groups.

The common feature between the results presented in this thesis and those for the homogeneous acid catalysed exchange of the alkyl benzenes ^{35,134, 135} is that the ring hydrogen atoms react in preference to side group atoms. However, there are a number of differences between the two systems. On these oxide catalysts the side groups in toluene and m-xylene neither enhance the rate of exchange of the ring atoms nor cause directing effects favouring reaction at the ortho or para positions. Furthermore, side group exchange does occur, although slowly, on these oxides but it is found only in exceptional cases in homogeneous acid catalysis e.g. with aromatic molecules containing the *t*-butyl side group ¹³⁶. The absence of any appreciable isomerisation of m-xylene at the temperatures used for ring exchange is important in relation to the equal reactivity of all four ring positions.

If isomerisation occurred at a rate comparable to exchange, examination of isotopic distributions would be insufficient to show up differences in the rate of reaction of the various ring positions since a binomial distribution of products would result irrespective of the relative activities. However, this is not the case as isomerisation is a much slower process than exchange on silica-alumina I and does not occur at all on silica-alumina II or alumina at temperatures where ring exchange is rapid. The conclusions drawn from inspection of isotopic distributions are therefore valid and the exchange results show what first happens to the hydrocarbon when it is chemisorbed on the catalyst surface.

In basis media Hall et al¹³⁷ using $K NH_2$ in liquid NH_3 , found that exchange of benzene and toluene was very slow and Shatenshtein and co-workers^{138,139} observed that the exchange of alkylbenzenes proceeds most easily when primary carbanions are formed, as they are more stable than secondary or tertiary ones. Exchange at the α position in toluene is about seven times faster than in ethylbenzene which is in turn five times faster than iso-propylbenzene. In alkali solution the hydrogen atoms on the ring and those joined to the α carbon atoms react at about the same rate¹⁴⁰. The displacement of electrons towards the ring and consequent increase in electron density of the ring in alkyl benzenes reduces the rate of exchange relative to benzene and ring exchange in toluene is about three times slower than in benzene. Exchange of hydrogen atoms on carbon atoms β to the ring can only be achieved by prolonged heating at higher temperatures.

temperatures.

Thus the reactions in alkaline media are diametrically opposed to those in acidic media. The results on silica-alumina and alumina lie somewhere in between these two extremes, more towards the acid side. It has been suggested that basic as well as acidic sites are present on silica-alumina ³⁰ and that reactions are favoured by a polarity within the surface. If this were so, then perhaps the results obtained here are what might be expected. However, there are other points concerning the mechanism of exchange and possible slow steps which may also effect the course of the reaction and they must be considered before strict comparisons with other systems can be made.

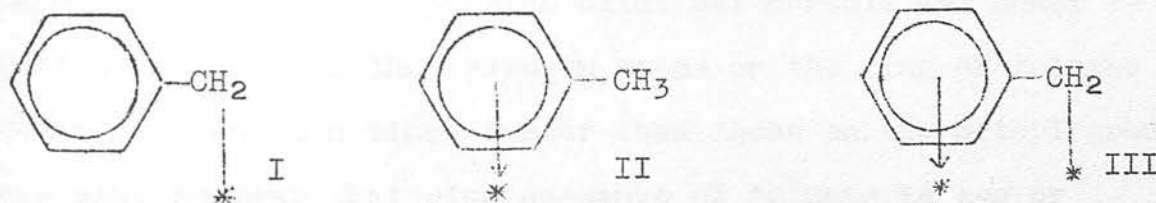
4.3 Comparison with Metals and Other Oxides

(a) Metals

The exchange behaviour of the alkyl benzenes over silica-alumina and alumina is strikingly different from the results found with metals and some other oxide catalyst. With metals the side group hydrogen atoms tend to exchange as fast if not faster than the ring atoms. There is also usually some evidence of multiple exchange and differences in reactivity among the various ring positions. Crawford and Kemball ⁴⁹ studied the catalytic exchange of alkylbenzenes with deuterium on nickel films. They found that with unsintered films the hydrogen atoms on carbon atoms α to the ring and in ring positions not ortho to a side group reacted most easily. The ring hydrogen atoms ortho to

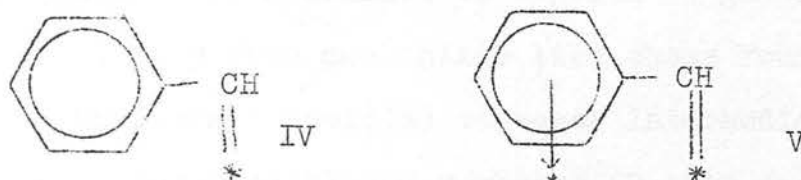
a side group were less reactive. They suggested that the easier exchange of the side group hydrogens was a consequence of the low bond dissociation energies of these carbon-hydrogen bonds which are some 20-25 Kcal/mole less than those for the other alkyl carbon-hydrogen bonds.

Horrex and Moyes ¹⁴¹ examined the exchange of toluene with deuterium on evaporated films of nickel, iron, palladium and platinum and found that toluene underwent exchange first in the side chain, then in the meta and para ring positions and finally in the ortho positions. These exchange reactions were also accompanied by hydrogenation reactions but in all cases exchange was the predominant process. Similar results were also obtained by Harper and Kemball ⁵⁰ for the exchange and deuteration of p-xylene on evaporated films of palladium, platinum and tungsten. The mechanism of exchange on metal catalysts is believed to involve adsorbed radicals. Adsorbed intermediates I, II and III were proposed by Crawford and Kemball to account for the exchange of alkyl benzenes over nickel ⁴⁹



Interconversion between the π -bonded species II and the $\pi + \sigma$ bonded species III can provide a mechanism for multiple exchange in which all the hydrogen atoms in the methyl groups are likely to take part. Species I gives rise to simple exchange.

In addition to these intermediates Harper and Kemball 50 propose two further intermediates IV and V to explain their results on platinum and tungsten.



The above surface intermediates lead to side group exchange.

For exchange of ring hydrogen atoms a number of intermediates have been proposed. These include all adsorbed species C_6H_n where n varies from 6 to 11. Those with $n = 6$ to $n = 9$ are π bonded to the metal surface. The species C_6H_{10} may be either π bonded ¹⁴² or σ bonded ³³. Although all these intermediates are arrived at by an associative mechanism it is also possible that exchange may occur by dissociative mechanism ¹⁴³ and as yet there is no experimental proof for either reaction path.

Other Oxides

On rutile (TiO_2) Lake and Kemball ⁵⁴ found that all the hydrogen atoms in toluene exchanged at similar rates by ^astepwise mechanism whereas on chromium oxide gel Burwell and Loner ⁵³ found that at $110^\circ C$ the hydrogen atoms on the ring of toluene exchanged about ten times faster than those on the methyl group. They also suggest that ring exchange of toluene is two or three times faster than benzene exchange. On partially deuterated hydrogen Y zeolites Venuto, Wu and Cattanach ¹⁴⁴ have recently reported that exchange of toluene at low temperatures leads to exclusive ring exchange, predominately in the ortho and

para positions, and that toluene was more active than benzene.

The mechanism of exchange of the alkyl benzenes on oxide catalysts are rather more difficult to explain in general terms since they seem to vary from mechanisms like those found in acid catalysis (Hydrogen Y zeolite) to cases intermediate between acid (or base) and metal catalysed exchange (Rutile and chromium oxide gel). The results on silica-alumina and alumina reported here also show this type of intermediate behaviour although, as stated previously the results are more like those found in homogeneous acid catalysis than in catalysis by metals.

The exchange of m-xylene with deuterium has now been studied on a number of catalysts and the results in Table 4.2 show the large range found for the ratio of ring to side group exchange. In general it seems that low ratios are found with catalysts such as the metals upon which adsorbed radicals are formed and large ratios are obtained with those oxides which would be more likely to give charged or highly polarised intermediates.

The results indicate that the exchange of m-xylene with deuterium may be a useful reaction for testing catalysts and for indicating the type of reactions which are likely to occur with hydrocarbon molecules.

4.4 The Mechanism of exchange on Alumina

The main facts which emerge from this work and previous

Table 4.2 Exchange of m-xylene with deuterium on catalysts

Catalysts	Temperature (°C)	Ring	Reference
		Side group exchange	
Pd film	0	10^{-4}	145
Sintered Ni film	20	10^{-2}	49
Ni X zeolite	170	10^{-1}	48
Fe, Pt or W films	0	~ 1	145
TiO ₂ (rutile)	400	3	54
Alumina	150	32	this work
silica-alumina II	100	70	" "
homogeneous acid	-	V. Large	136

work with this catalyst are as follows:

- (a) The exchange between hydrogen and deuterium ^{105,127} takes place readily at low temperatures and consequently there is no difficulty about "activating" the hydrogen molecules for this particular exchange
- (b) The rate of exchange of CD₄ with hydrogen ¹²⁷ is close to the common rate found in this work for the exchange of the ring hydrogen atoms in the three aromatic molecules. The rate of the methane reaction at 20°C is 5.4×10^9 mol/sec/cm² compared with 3.7×10^9 in the same units for benzene exchange. The

activation energies for both reactions are also similar (5.7 and 6.0 Kcal/mole for methane and benzene respectively).

(c) The surface hydroxyl groups on the catalyst exchange with deuterium much more slowly than the rate of the hydrogen/deuterium reaction. Temperatures of 50°C to 100°C or even higher are needed to bring about the replacement of the hydrogen associated with the surface ¹⁰⁵⁻¹⁰⁷. An approximate activation energy of 6 Kcal/mole has been derived for the process ¹⁰⁶ but evidence based on spectroscopic studies showed that there is a range of rates for the replacement of different types of hydroxyl groups ¹⁰⁷.

(d) When CD₄ is used as the source of deuterium atoms only a fraction of the surface hydroxyl groups exchange rapidly at 135°C which is a much higher temperature than that required for the exchange of methane with deuterium or for the equilibration of CH₄ and CD₄ ¹²⁷. The sites which exchange readily at 135°C number $7 \times 10^{12}/\text{cm}^2$.

(e) Ethylene exchanges on a deuterated and evacuated alumina catalyst by a stepwise mechanism but if D₂O is added after evacuation the rate of exchange decreases and multiple exchange takes place ¹⁰⁸.

Larson and Hall ¹²⁷ suggested that the cleavage of a carbon-hydrogen bond in methane was the slow step in the exchange reactions of methane. If a corresponding process which would probably be the formation of a new carbon-hydrogen bond for the exchange of ring atoms was rate determining in the results

reported here it must be chance that both methane and the alkylaromatics exchange with deuterium at much the same rate. However, another possibility might be considered. The exchange of a hydrocarbon may only take place readily with deuterium atoms which are present in the form of OD groups at special sites on the catalyst surface. Effective stepwise exchange would result irrespective of the mode of adsorption of the hydrocarbon and the number of times it exchanged its 'hydrogen' with the neighbouring OD(OH) group if the hydrocarbon desorbed before more deuterium could be supplied to the system by exchange of these catalysts OH groups with deuterium from the gas phase. Since this mechanism implies that the rate of reaction is controlled by the rate of exchange of the surface OH groups on the active sites this suggestion affords a simple explanation for the following

- 1) the stepwise exchange of the benzene, toluene and m-xylene ring hydrogens.
- 2) the equality between the rates of exchange of the ring atoms in the three aromatic molecules on any one catalyst.
- 3) the similar rates found for exchange of methane ¹²⁷.
- 4) the absence of directing effects due to the side groups in the aromatic molecules.
- 5) the similarity between the activation energies of the exchange reactions and the approximate value for the replacement of surface hydroxyl by deuterium ¹⁰⁶.

6) the results obtained by Kloosterzeil ¹⁰⁸ for exchange of ethylene. The stepwise exchange at low D₂O contents could be due to this rate determining step and the presence of multiple exchange at higher D₂O contents due to the increased availability of surface deuterium enabling the adsorbed ethylene to obtain more than one deuterium atom per sojourn to the catalyst surface.

However, for this hypothesis to be tenable it is necessary to assume that a relatively small number of these special sites exist in order to account for the absence of an initial burst of reaction with toluene exchanged on a catalyst pretreated with deuterium at 520°C. In this run all the exchangeable OH groups left after evacuation would have been replaced by OD groups and so on admission of the toluene mixture, the initial rate of reaction would not be controlled by the exchange rate of surface hydroxyls. Thus, if as assumed in the above mechanism, the rate of exchange of the hydrocarbon with a neighbouring OD group (a), is faster than the rate of regeneration of the OD groups by exchange with deuterium gas (b), one would expect to see an initial fast rate indicative of process (a) levelling out to a steady state controlled by process (b). As mentioned above no such initial fast rate was detected experimentally. This would not invalidate the above assumptions, however, if the number of active sites were small since calculations show that if there were only about 10¹¹ such sites/cm² of catalyst surface the initial fast rate would only extend over a small

portion of the reaction (0.4%) and would not be detected experimentally. On the other hand, an assumption of less than 3×10^{12} sites/cm² would be difficult to reconcile with the data from the poisoning experiments carried out by Larson and Hall¹²⁷ which should make this initial fast rate extend over the first 12% reaction and should be easily recognisable.

Alternatively, the absence of directing effects in the exchange of toluene and *m*-xylene could be explained if the reaction proceeded by a mechanism whereby the aromatic ring is bound to the surface by donation of π electrons to electron acceptor (Lewis acid) centres prior to exchange with deuterium. In the homogeneous acid catalysed exchange of the alkyl benzenes, where electronic effects are very pronounced the mechanism is believed to involve simple electrophilic attack by protons which will naturally attach themselves to the ring positions having the highest electron density. If, as may be the case on alumina, the benzene ring is π bonded to the surface prior to exchange the electron densities at the various ring positions will be different from those found in isolated gas phase molecules, and one might expect all the ring positions to be made equivalent in this respect, so that no preference for reaction at any particular position will be found. The exchange of this adsorbed molecule with deuterium may then proceed by an addition elimination reaction with consequent desorption.

The equal reactivity of the ring hydrogens in benzene,

toluene and *m*-xylene can also be accounted for if the electron donating effects of the methyl groups are all transmitted to the π bond. This would affect the strength of the π bond, but would leave the charge distribution on the ring similar to that found with π bonded benzene. Thus the presence of methyl groups may not influence the rate of the addition elimination reaction and if one assumes this reaction to be rate determining the differences in the strengths of the π bonds will not influence the overall rate of reaction.

Another effect which should be considered in these reactions is the influence of the field gradients near the catalyst surface. These gradients may distort polarizable molecules and thus play an important role in the nature of the exchange reaction. However, on a deuterated hydrogen Y zeolite, which possesses large field gradients toluene was still found to exchange predominantly in the ortho and para positions ¹⁴⁴ and so it seems unlikely that the smaller field gradients present on alumina are pronounced enough to be by themselves responsible for the absence of directing effects in the exchange of toluene and *m*-xylene.

The slow step in the exchange of the side groups must be associated with the activation of the hydrocarbon and the exchange is likely to occur by a dissociative mechanism possibly involving heterolytic cleavage of a carbon hydrogen bond.

Results with a wider range of alkyl benzenes including ethylbenzene and cumene would be useful in determining the mechanism of these reactions.

Finally it has also been suggested ^{97,98,146} that gas phase or chemisorbed oxygen enters into some reactions on alumina promoting the reaction. This is not the case with the results reported here, since experiments where the catalyst had been cooled to room temperature in oxygen gave no increase in rate over that for a normal run without this oxygen treatment. There was in fact a decrease in rate which was attributed to the adsorption of poisons inadvertently introduced to the catalyst along with the oxygen and thus in these reactions, as for hydrogen - deuterium exchange,¹⁰⁵ the catalyst activity does not seem to be due to oxygen deficiencies, but rather may be caused by the strained high energy surface cause by dehydration. Possible mechanisms for these reactions have been outlined above but further experiments need to be carried out before the slow step is positively decided upon.

4.5 The reaction on Silica-alumina I

The chief point which is worth noting here is that this catalyst is much less active than alumina for the exchange reactions of hydrogen and of the alkylbenzenes with deuterium. In this respect these results are in accord with other data for silica-aluminas containing 10% to 13% alumina which show poor activity for exchange reactions of methane and low rates of replacement

of surface hydrogen by deuterium ¹²⁷.

On silica-alumina containing 12.5% Al_2O_3 Larson and Hall ¹²⁷ have shown that CD_4 exchanges its deuterium atoms with the catalyst hydrogen in the temperature range 460–540°C, but the direct exchange between CD_4 and CH_4 does not take place in contrast to the results with alumina where this reaction occurs readily at room temperature. With silica alumina I the exchange of hydrogen with deuterium is only slightly more rapid than the reaction of the ring atoms of the alkylbenzenes but the latter exchange much more rapidly than methane in contrast to the results with alumina. Larson and Hall's results for the exchange of methane d_4 with the catalyst hydroxyl groups are about 100 times slower at 490°C than those reported here for exchange of alkyl benzenes with deuterium. The activation energy for the methane reaction is 33 Kcal/mole which is much higher than that for the alkyl benzene reaction (10 Kcal/mole).

Much of the previous work on exchange reactions using silica-alumina ^{67,126,129,130,147,148} has involved pretreating the catalyst with (or adding) D_2O and examining the exchange between the reactant molecules and the adsorbed D_2O . Any close comparison of these results with ones using deuterium gas may be misleading since the presence of water on the catalyst surface influences ^{the} ~~into~~ exchange behaviour. It has been shown ¹⁰⁸ for example, on alumina, that multiple exchange takes place if D_2O is adsorbed on the catalyst, but exchange is

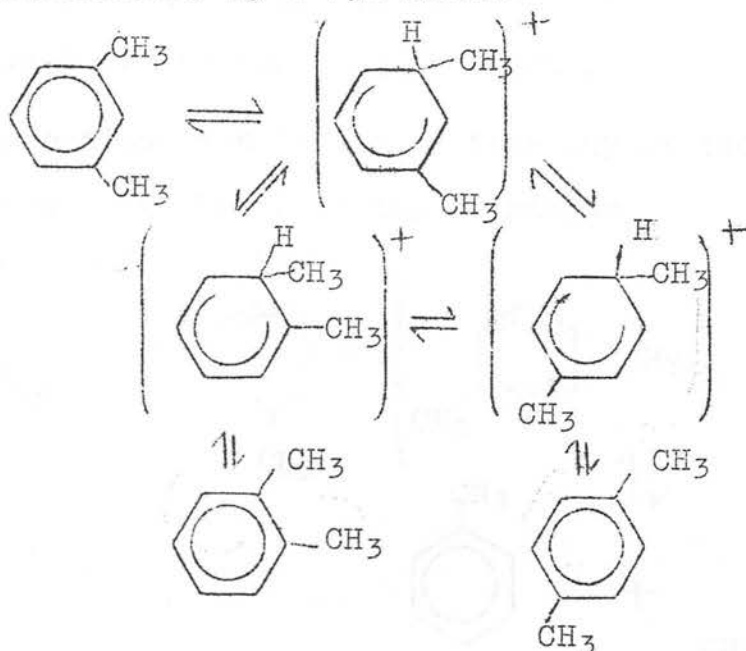
stepwise if ethylene is exchanged with a deuterated and evacuated catalyst. On silica-alumina the amount of D_2O adsorbed on the catalyst influences the rate of reaction and there is usually a maximum in the curve relating to heavy water content. Small amounts of heavy water accelerate the reaction, but have a poisoning effect if present in appreciable quantity. Using D_2O adsorbed on silica-alumina Hansford et al.¹³⁰ found the order of exchange activity of different molecules to be olefins > saturated hydrocarbons containing tertiary carbon atoms > benzene > hydrogen > saturated hydrocarbons without tertiary carbon atoms. These results indicate that the ease with which the hydrocarbon can form carbonium ions is an important factor in exchange.

Perhaps the most enlightening result here in connection with what has been said about the reaction mechanism on alumina, is the fact that on silica-alumina there is a type of surface deuterium readily formed from heavy water which reacts more rapidly with some hydrocarbons, including benzene, than with hydrogen. This latter point, and the fact that the activation energy for the hydrogen reaction is the same as that found for the exchange of the alkyl benzenes (10 Kcal/mole), lends some support to the idea that a rate determining step in the exchange of alkyl benzenes with deuterium on silica-alumina I might be, as on alumina, the conversion of OH to OD at suitable sites. This would explain the large decrease in rate observed

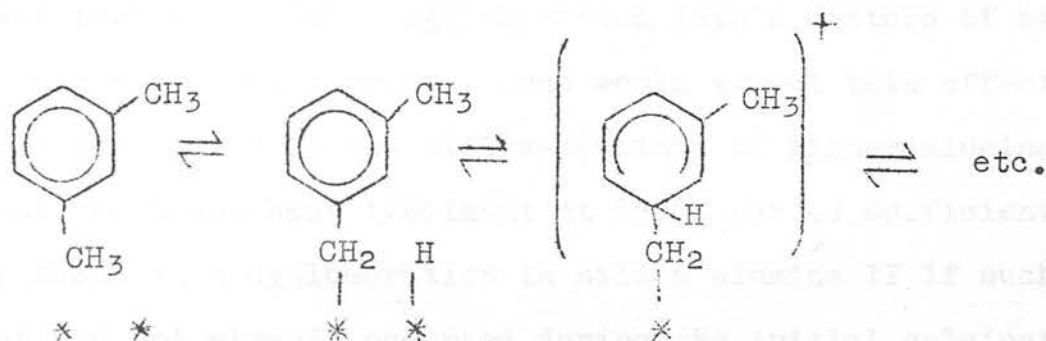
in raising the outgassing temperature from 520°C to 660°C. As the temperature of outgassing is increased the number of OH groups on the surface will decrease due to the elimination of water and thus the number of active sites will also decrease. Similar outgassing effects were noticed by Hindin, Mills and Oblad ¹²⁶ on the exchange rate of isobutane on a deuterated silica-alumina. The increase in rate on back addition of small amounts of water could thus be due to the creation of extra active sites for exchange which may, however, be rendered inactive by adsorption of larger amounts of water leading to the decrease in rate observed. These ideas would suggest that in the reactions of methane on silica-alumina ¹²⁷ the rate determining step is the rupture of the CH bond since this reaction is much slower than the exchange of the alkyl benzenes and has a much higher activation energy, similar in fact to that found for exchange of methane on metals, where a dissociative mechanism is operative.

It is interesting to note that side group exchange and the isomerisation of *m*-xylene have comparable rates and activation energies and hence possibly a common mechanism is operative. Positional isomerisation of the xylenes can be accomplished at less than 100°C in the presence of strong acids such as aluminium chloride ^{149,150}. Other workers ¹¹⁶ have found silica-alumina will catalyse this reaction at about 550°C. The mechanism of isomerisation ¹⁵¹ has been explained by the addition of a proton at the ring carbon atom holding the alkyl group to form a sigma

complex. The methyl group being thus less firmly held can then move intramolecularly by a 1,2 shift.



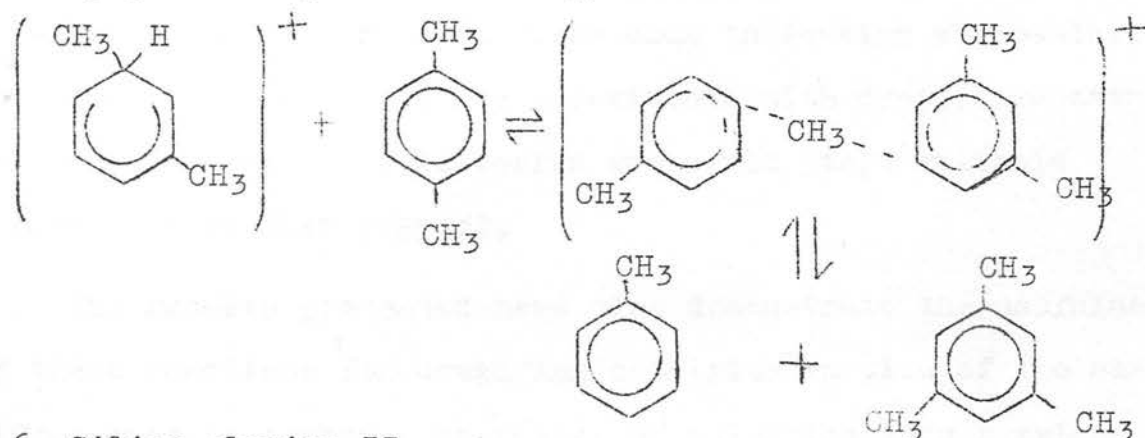
From this mechanism alone it is difficult to envisage side group exchange occurring along with isomerisation. However, before attack at the tertiary carbon atom takes place, the molecule may be dissociatively adsorbed as depicted below:



This mechanism would lead to exchange and isomerisation. Both processes will occur at the same rate if the slow step is associated with the adsorption/desorption of the hydrocarbon molecule.

Only the strongest acid sites may be capable of catalysing this reaction. This would explain the low rates compared with those found for exchange of the ring hydrogens.

Disproportionation is slower than any of these processes and may proceed by the following mechanism



4.6 Silica-alumina II

This catalyst behaved more like alumina than silica-alumina I in every respect and it is probable that a separate alumina phase is present. Hansford ⁶⁸ suggests that when silica-alumina is heat treated to 760°C agglomeration into a mixture of silica and alumina particles occur. One would expect this effect to be more pronounced in the silica-aluminas of higher alumina content and hence heat treatment at 520°C may be sufficient to bring about this agglomeration in silica alumina II if such an effect had not already occurred during the initial calcination of the catalyst after preparation ⁶⁴.

The activation energies for the exchange of the ring atoms are similar on both silica-alumina II and alumina and the

higher activity of the former may be associated with a greater number of catalytic sites.

4.7. Conclusion

Although it is premature to speculate further about the mechanism by which exchange may occur on these catalysts the results presented here have given some indication of possible slow steps. Other exchange experiments with deuterated catalysts and in the presence of deuterium gas could yield valuable information in this respect.

The results presented here also demonstrate the usefulness of these reactions for comparing catalysts in view of the marked differences in exchange character of molecules like m-xylene as one proceeds through the series of catalysts from pure metals to acidic oxides and on to true acid catalyst. Since these exchange reactions occur at temperatures below those required for other chemical reactions, the results from exchange experiments yield information concerning the initial processes undergone by the hydrocarbon but in some cases, as has been demonstrated above, care is needed in the interpretation of the results.

PART III

THE EXCHANGE OF HYDROGEN WITH DEUTERIUM AND
HYDROCARBONS WITH HEAVY WATER ON ION EXCHANGED
X TYPE ZEOLITES.

CHAPTER I

Introduction1.1 Synthesis of molecular sieve zeolites

The best known occurrence of zeolite minerals is in the cavities and amygdules of basaltic and dibasic igneous rocks and over 40 different species have been recognised 152, 153. The molecular sieve action of these crystalline zeolites (alumino-silicates) is due to their structure. They are composed of definite arrangements of SiO_4 or AlO_4 tetrahedra which are built into more complex structural units, often polyhedra. These polyhedra may have considerable cavities at their centres, while the stacking of the polyhedra can create new and larger cavities. Pores or windows open into and connect the cavities. For any particular type of such zeolite, these pores are precisely uniform in diameter and it is because of this feature that the name 'molecular sieves' has been given to them, since the diameter of the pores determines the molecular sieve properties of each type, enabling it to adsorb selectively, only those molecules which are capable of entering the pores. By sharing oxygen atoms, the polyhedra assume three dimensional structures which often display remarkable rigidity and permanence though permeated by cavities interconnected by pores. The volume of the cavities may be 50% or more of the volume of the crystal.

Attracted by the potential application of crystalline

zeolites to the separation of gases, the Linde Division of the Union Carbide Corporation in 1943 initiated a study of zeolite mineral synthesis and characterisation. By 1952 many different species of synthetic zeolite had been prepared ⁿ154, 155. The Linde approach to the synthesis of molecular sieves was to use a freshly prepared, highly reactive, alumino-silicate gels prepared from aqueous solutions of sodium aluminate, sodium silicate and sodium hydroxide. The sodium zeolites result when the gels are crystallized at temperatures ranging from room temperature to 150°C at atmospheric or autogeneous pressure ¹⁵⁶. The gel structure is produced by the polymerisation of the aluminate and the silicate anions. During the crystallisation of the gel, the sodium ions and aluminate and silicate components apparently undergo a rearrangement into an ordered crystalline structure. This comes about by a de-polymerisation of the gel, due to the hydroxyl ions present in the reaction mixture (as sodium hydroxide). These are the basis for the zeolite crystals and as large numbers of crystallite nuclei are formed from the supersaturated gels the final product consists of a finely divided white powder of very small crystals, usually only a few microns in size.

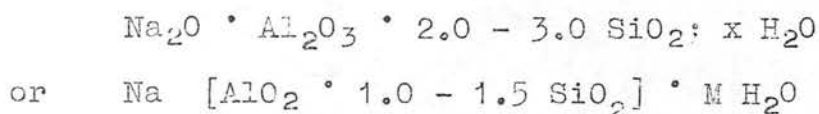
About 30 species of zeolites have been prepared in a pure state as a result of the controlled variation of parameters such as the initial composition of the gel, crystallisation temperature and type of reactant. Some of these synthetic

species appear to be structurally related to natural zeolites; others appear to have no known analog among the group of naturally occurring forms. The most commonly used forms of these synthetic crystalline alumino-silicates are code named A, X and Y. The A-type sieves have a Si/Al ratio of about 1.0 with openings to the large channel systems of 4.2 Å diameter and are commonly used for the drying of gases. The X-type sieves have a Si/Al ratio of about 1.2 and openings of 8 Å diameter. The Y-type sieves have similar pore dimensions and crystal structures to that found in the X sieves but have a larger Si/Al ratio (~ 2.5). Both the X and Y forms of molecular sieve are of catalytic interest. The work in this thesis concerned with zeolites has been carried out using the X type of sieve and further discussion where possible will be confined mainly to this one type.

1.2. Crystalline Structure

The structures of X and A sieves have been studied in considerable detail 157-159. These structures consist of a three dimensional framework of SiO_4 and AlO_4 tetrahedra. The aluminium ion is small enough to occupy the position in the centre of the tetrahedron of four oxygen atoms, and the substitution of Al^{3+} for Si^{4+} in framework silicates is common. However, each substitution requires the presence of a metal ion such as Na^+ or Ca^{++} in order to maintain electrical neutrality.

The structure of NaX, i.e. an X type sieve where the cation included during synthesis is Na^+ , is closely related to that of the mineral faujasite ¹⁶⁰. The chemical composition of NaX can be written as:



This type of formulation shows that the Si/Al ratio can vary between certain limits, that the Na/Al ratio is unity and that the amount of water in the structure can vary.

The structures of many zeolites consist of simple arrangements of polyhedra, each polyhedron itself consisting of a three-dimensional array of $(\text{SiO}_4, \text{AlO}_4)$ tetrahedra in a definite geometric form. The sodalite group of zeolites, which include zeolites A, X and Y are all based on frameworks which are simple arrangements of truncated octahedra sometimes called cubooctahedra. The tetrahedra are arranged at the corner of the truncated octahedra which, in keeping with Euler's theorem, contains 8 hexagonal faces, 6 square faces, 24 vertices and 36 edges (Figure 1.1). These cubooctahedra, which are similar to those found in the mineral sodalite and sometimes are referred to as sodalite cages, contain small cavities which define the so called β -cages of the zeolite structure. These cavities have a free diameter of 6.6 Å and openings, through the hexagonal faces, of 2.2 Å.

The different types of zeolites result from the various

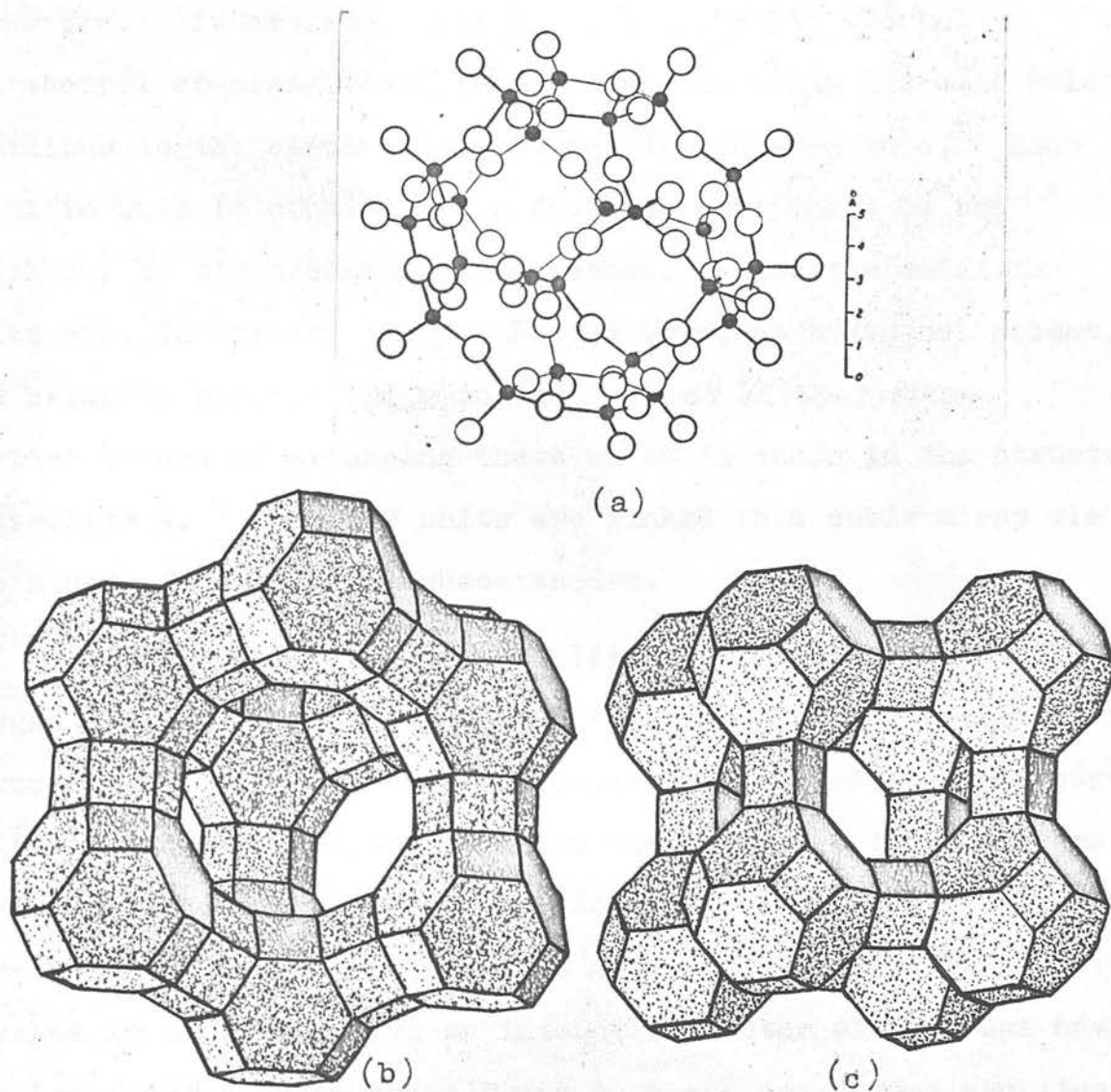


Figure 1.1

- (a) Structural arrangement of atoms in the sodalite cage,
 • Al or Si, O oxygen ¹⁶¹.
- (b) (c) Arrangement of sodalite cages or truncated octahedra
 in the framework structures of Linde X (b) and Linde A
 (c) zeolites ¹⁶².

ways in which these sodalite units are arranged in the crystal structure. In zeolites type X and Y the units are in tetrahedral co-ordination, the centres occupying the same relative positions as the carbon atoms in the diamond structure. Each sodalite unit is connected via the hexagonal faces to its neighbour by six bridging oxygen atoms. Thus the sodalite units are, in effect, interconnected by squat hexagonal prisms, the bridging oxygens lying on the 'walls' of the prisms. Another method of arranging these units is shown in the structure of zeolite A. Here the units are linked in a cubic array via the square faces of the cubooctahedra.

The co-ordination of the sodalite units via interconnecting oxygen atoms automatically generates much larger cages in the structure. These are referred to as the α -cages. The α -cages in the X and Y sieves are 26-hedra and again are in tetrahedral co-ordination. They have a free internal diameter of $\sim 12 \text{ \AA}$ and openings to the other cages of $\sim 8 \text{ \AA}$ via 12 membered rings. The α cages in zeolite A have an internal diameter of $\sim 11 \text{ \AA}$ but have smaller openings than those found in the X and Y type zeolites ($\sim 4.2 \text{ \AA}$).

Figure 1.1 shows diagrammatically the way in which the cubooctahedra are stacked in the zeolites A and X.

1.3 Ion Exchange

Smith ¹⁶³ defined a zeolite as "an alumino - silicate with a framework structure enclosing cavities occupied by large ions

and water molecules, both of which have considerable freedom of movement, permitting ion exchange and reversible dehydration". The ability of zeolites to undergo cation exchange was one of the earliest properties recognised and a wide range of ion exchange character has been observed ¹⁶⁴, ¹⁶⁵,. Ion exchange of these zeolites is also accompanied by changes in the unit-cell dimensions of the crystal, although the variations are usually small. Barrer ¹⁶⁵, ¹⁶⁶ has shown that in faujasite the lattice constant changes from 24.9 Å to about 25.6 Å on replacing the monovalent sodium ions by divalent nickel or cobalt ions. The theoretical cation exchange capacities for the synthetic zeolites are quite high amounting to about 4.7 milliequivalents/gram of hydrated NaX, the extent of exchange tending to diminish, in the inorganic series of ions, with increasing Debye-Huckel parameter, a , of the ions. This is easily understandable in terms of the essentially electrostatic cation-anion bond. Provided that the exchanging cation can enter the channel system of the sieve, ion exchange can occur.

Thus, many types of ion exchanged zeolites can be prepared although complete substitution of one ion for another is not always possible without destroying the zeolite structure. Complex cations can be introduced into the structure ¹⁶⁵ provided they can enter the zeolite pores. Exchange should be carried out in alkaline solution since if the pH of a zeolite/water suspension is reduced below 5 aluminium ions are removed

from the framework and the structure is destroyed. The pH of a zeolite/water solution alone is generally above 7 due to a limited amount of hydrolysis ¹⁶⁷. Thus the cations in zeolites cannot be replaced by protons on treatment with aqueous acids. However, a hydrogen or proton form of molecular sieve zeolites can be prepared to a limited extent by first exchanging the alkali metal ions with ammonium ions. Subsequent heating of this ammonium form at temperatures above 350°C liberates ammonia with the consequent ^eformation of protons which are required to neutralise the negative charge on the zeolite framework. This process called 'decationisation' has been studied in some detail ^{168, 169}. The proton is thought to be attached to a framework oxygen atom forming a Lewis acid type site, rather than ^aremaining mobile. The protons can be removed on further heating to form a dehydroxylated zeolite with the formation of very strong electrophilic (defect) sites.

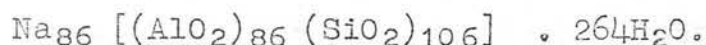
Other forms of zeolite can also be prepared. The cations present in the sieve can be reduced under certain conditions to the elemental form, or unusual valence states. Extremely high dispersions of metal atoms can be obtained in this manner ^{170, 171}.

1.4 Cation Locations

In zeolites X and Y the number of aluminium ions per unit cell is given by ¹⁷²:

$$N_{Al} = \frac{192}{(1+R)} \quad \text{where } R = \frac{N_{Si}}{N_{Al}}$$

The number of aluminium atoms (N_{Al}) per unit cell of zeolite X varies from 96 to about 77 (76 to 48 for zeolite Y). For each aluminium tetrahedrally co-ordinated in the zeolite crystals an equal number of positive ions must be present to preserve electrical neutrality. The positive ions are usually present as monovalent or divalent cations and a typical formula for the hydrated unit cell of NaX is:



The position of these cations in the crystal structure has been studied in some detail by Breck ¹⁵⁸, ¹⁶⁷ and Shoemaker et al ¹⁵⁹, ¹⁷⁰. In zeolites type X and Y three distinct cation sites are recognised.

Site I These sites are located in the centres of the hexagonal prisms joining two sodalite units. The cation has six oxygen atoms at $2.74 \overset{\circ}{\text{\AA}}$ as nearest neighbours with six more at a somewhat greater distance. There are 16 of these sites per unit cell.

Site II There are 32 of these sites per unit cell situated at or near the centres of the six membered rings on the sodalite cages which are exposed to the interior channels of the crystal. The nearest neighbours to these cation sites are three oxygen atoms at a distance of $2.49 \overset{\circ}{\text{\AA}}$ with three more slightly further away. For small cations the oxygens form a distorted octahedral site. Larger cations may lie inside or outside the sodalite cages.

Site III There are 48 of these sites per unit cell at the centre of the four membered rings on the channel walls. There are two oxygens as nearest neighbours.

Other sites have been proposed in addition to those above such as those in the β cages adjacent to S. II. These additional sites, however, seem rather to be modifications of the three basic sites above rather than new sites.

Broussard and Schoemaker ¹⁵⁹ in X-ray crystal structure studies on hydrated zeolite X powder assumed two cation positions, Na_1 and Na_2 , corresponding to sites I and II above. The reported differences in sodium ion positions between hydrated NaX and its naturally occurring analog, faujasite, should be noted. From the single crystal studies of Baur ¹⁷³ site I is not occupied in the sodium rich form of hydrated faujasite. Broussard and Shoemaker found in their study of hydrated NaX that site I was essentially fully occupied by sodium ions. X-ray diffraction studies on faujasite single crystals ¹⁷⁴ which were treated with aqueous calcium salt solutions and then dehydrated, have shown that the calcium ions occupy site I in preference to site II. No occupation of site III is necessary to obtain electrostatic neutrality within the crystal. Angell and Schaffer ¹⁷⁵ have shown that carbon monoxide adsorbed on X type zeolites containing divalent cations gives rise to a cation - specific infra-red stretching band. Univalent cations do not give this extra high frequency CO band ($2170 - 2210 \text{ cm}^{-1}$), and so

the appearance of this band is taken as an indication of divalent ions in surface sites, CO being unable to penetrate to site I because of its size. Using this technique coupled with measurements of the heat of adsorption of CO they found that on exchange of NaX with Ca^{++} ions the Ca^{++} entered site I preferentially and only after about 35% of the Na^+ ions had been replaced did the Ca^{++} ions occupy surface sites accessible to CO molecules, (site II and III). However, after about 20% exchange of the Na^+ ions for Co^{++} and Ni^{++} ions the high frequency infrared bands appeared, indicating that Co^{++} and Ni^{++} cations were in surface sites. Thus the strength of site preference exhibited depends on the cations being used.

Barry and Lay ¹⁷⁶ have used the E.S.R. spectra of Mn^{++} in X zeolites, pre-exchanged with diamagnetic cations, to indicate the possible distribution of cations under certain conditions of hydration. They found that Mn^{++} ions could occupy a number of different sites and was assumed not to have a very strong relative site preference. This being so, they concluded from their results that in the hydrated K^+ , Na^+ , Ca^{++} and La^{+++} X sieves the cations preferred site I to sites II and III while Li^+ , Mg^{++} and Zn^{++} X sieves prefer sites II and III to site I.

In dehydrated samples heated at 200° , 300° and 400° the order of preference of the alkali metal ions for sites II and III is $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$, showing the more electropositive cations have a stronger preference for site I. However, the Zn^{++}

cation was found to have a marked preference under all conditions for site II. The Zn^{++} in ZnO is in tetrahedral co-ordination and thus it would not be expected to favour the octahedral co-ordination offered by Site I. It may be possible for a cation in sites II or III to achieve tetrahedral co-ordination in the hydrated state by localisation of water molecules. Since Mg^{++} in MgO has octahedral co-ordination, this ion may be expected to favour Site I and this seems to be the case in a $\text{NaX/Mg}^{++}\text{Mn}^{++}$ sieve which was heated to 300°C .

Contrary to expectations the La^{+++} ion seems to favour site II. Being a strongly ionic cation it would be expected to favour the high co-ordination of site I. Barry and Lay offer three possible reasons why La^{+++} remains preferentially in site II

- 1) The La^{+++} may be stabilised in site II if residual water or hydroxyl groups are present.
- 2) The configuration of minimum free energy may be one in which the La^{+++} ions are most separated, which is obtained if the ions occupy site II (90% exchanged sample).
- 3) There may be a high activation energy for migration of La^{+++} ions.

Rabo ¹⁷⁰ suggests that with tervalent ions the effective electrostatic field may become strong enough on dehydration to cause hydrolysis and Ward and Habgood ¹⁷⁷ have suggested that this may also occur with Magnesium sieves giving MgOH^+

Table 1.1 suggested site preference for cations in X type sieves

Sieve Cation	Cation Radius ° Pauling A	Maximum Possible Exchange (Literature)	Hydrated		Dehydrated	
			S _I Preference	S _{II} , S _{III} Preference	S _I Preference	S _{II} , S _{III} Preference
UO ₂ ²⁺	1.8-1.9	50	No entry due to size	W	No entry due to size	W
Cs ⁺ , Rb ⁺	1.69, 1.48	60				
Tl ⁺ , K ⁺	1.44, 1.33	100	S	A	S	A
Pb ²⁺ , Ag ⁺	1.32, 1.26	100	S	A	S	A
Sr ²⁺ , Cd ²⁺	1.13, 0.97	95	A	A	S	A
Ca ²⁺						
La ³⁺ , Ce ³⁺	1.15, 1.10	90	W	S	S	A
Mn ²⁺	0.82	90	A	A	A	A
Ni ²⁺	0.78	80				
Zn ²⁺	0.74	90	W	S	W	S
Mg ²⁺	0.65	76	A	A	S	W
Li ⁺	0.60	90	W	S	W	S

W = weak

A = Average

S = strong

The suggested site preference for different ions under different conditions is shown in Table 1.1. These preferences are in no way conclusive and only give a general picture that one might draw from the evidence available.

1.5 Dehydration and Stability

When water molecules are removed from the zeolite X by the application of heat in a reasonably good vacuum, there is no appreciable change in the basic framework structure even under stringent conditions. The water molecules do affect the specific positions of exchangeable cations, but they do not appear to have any primary structural function and can thus be removed reversibly without disrupting the framework structure. The desorption of water is continuous and no steps are shown in the pressure - temperature plots. After dehydration zeolite X is remarkably stable to heat. Breck and Flanigen ¹⁷² have reported that X-ray ^dpower diffraction patterns of zeolite X after heating for several hours at 700° revealed no structural change; after 36 hours at 760° the zeolite was converted to a residue which was mostly amorphous. The differential thermal curve of zeolite X exhibited a continuous loss of water over a broad range, commencing slightly above room temperature to about 350° with a maximum at about 250°. Sharp exothermic peaks at 772° and 933° indicated recrystallisation to other phases (carnegeite and nepheline - like phases respectively).

Many zeolites are known to undergo structural degradation

when subjected to water vapour at elevated temperatures. Breck and Flanigen ¹⁷² report that NaX, on being subjected to steam at 410° and 1 atm pressure for 3 hours, showed essentially no zeolite crystallinity. However, this effect varied with the Si/Al ratio of the zeolite, the higher Si/Al ratio samples being more stable; NaY showed essentially no loss in zeolite crystallinity after the above treatment. The cation present also affects stability. Barrer and Bratt ¹⁷⁸ found an appreciably lower thermal stability for Sr - exchanged X and Co - exchanged X than other monovalent and divalent forms. These authors have also measured the sorption equilibria, kinetics of water loss and the differential heats and entropies of water and ammonia in ion exchanged near faujasites as well as determining the relative importance of cations and anionic framework in determining the energetics of zeolitic water.

1.6 Adsorption Properties

The crystalline solid remaining after dehydration of a zeolite is a highly selective adsorbent for gases and vapours. The molecular sized voids which permeate the crystals form an internal surface or adsorption space. When exposed to a gas or vapour, the zeolite cavities fill rapidly with the molecular species concerned, provided the molecules are small enough to enter into the channels, and when the filling is complete no more adsorption occurs. This leads to a rectangular type of adsorption isotherm. This internal volume of the zeolite

crystals is not available to molecules which are too large to enter into the channel systems through the cage 'windows'.

The adsorption capacities of zeolites for many compounds have been determined ^{172, 167, 179}. The capacities of zeolite X for a number of molecules with a range of diameters are listed in Table 1.2 together with data for zeolite A for the sake of comparison. An estimate of the size of the zeolite channels can be obtained from adsorption data for a number of tertiary amines. If the kinetic diameter of the amine molecule is too large to enter the channel system then this molecule will not be adsorbed on the channel walls. Using this technique Breck and Flanigen ¹⁷² have shown that the effective pore diameter of NaX is about 9 - 10 Å whereas in calcium or barium exchanged X sieves the diameter is reduced to 8 - 9 Å. Thus the diameter can be varied slightly by ion exchange.

There are many examples of the selective adsorption character shown by dehydrated zeolite crystals ^{34-39, 179}. For example, ethane (~ 4 Å diameter) is adsorbed on NaA (type 4 A) but butane (~ 5 Å diameter) is excluded. Ca A (type 5 A) has larger pore openings and will adsorb straight chain hydrocarbons, but not branched chain or cyclic hydrocarbons. NaX will adsorb many branched chain and cyclic materials in addition to everything adsorbed by Na A and Ca A. As shown in Table 1.2 NaX has a higher affinity for oxygen than nitrogen. Although the nitrogen molecule is only 0.2 Å larger than oxygen

Table 1.2 Typical Adsorption Capacities of Zeolites

ADSORBATE	KINETIC DIAMETER Å	TEMP °C	PRESSURE mm Hg	No. of adsorbed molecules/cavity	
				NaX	NaA
H ₂ O	2.65	25	25	33	29
Ar	3.40	-183	760	17.6	14 - 16
O ₂	3.46	-183	760	18.6	14 - 16
Kr	3.60	-183	17	14.5	
N ₂	3.64	-196	700	16.6	14 - 16
Xe	3.96	-78	700	9.3	
n-pentane	4.3	25	205	4.3	
cyclohexane	6.0	25	45	3.9	—
Benzene	6.0	25	76	5.6	—
neopentane	6.2	25	700	3.6	—
(C ₄ H ₉) ₃ N	8.1	25	1	2.1	—
(C ₄ F ₉) ₃ N	10.2	50	0.55	(0.1)	—

the difference is sufficient to enable the sieve to discriminate between them ¹⁶⁷.

Molecules can also be trapped in zeolites like a clathrate type of complex. These molecules can be forced into the pores at elevated temperatures and pressures. When quenched the resultant reduction in zeolite pore size, due to the reduction in vibrational amplitude of the oxygen atoms on the pore openings, is sufficient to trap the molecules in the structure. In this way methane, ethane, argon and krypton can be 'encapsulated' in NaA.

The special adsorption properties of molecular sieves can be summarised as follows.

- 1) They adsorb small molecules and reject those greater than their pores can retain.
- 2) They have a high adsorption capacity at low adsorbate concentrations.
- 3) They have a high adsorption capacity at elevated temperatures.
- 4) They have an unusually high affinity for unsaturated organic compounds.
- 5) They have ~~an~~ unusually high affinity for polar molecules
- 6) They will adsorb water in preference to other adsorbates under a wide range of conditions.

The adsorption characteristics of molecular sieves can be varied by ion exchange, Si/Al composition and other structural

alterations and can thus be tailored for specific purposes, many of which have industrial applications.

1.7 Catalytic Properties

The molecular sieve zeolites of primary interest to investigators as catalysts have been the type X and the type Y. In the many varied forms in which they can be prepared, they have been found to be excellent catalysts for many reactions. Some of the reactions studied are given below:

Cracking reactions

Zeolite catalysts exhibit high cracking activity with paraffin and olefin hydrocarbons. Paraffin cracking on NaX zeolite exceeds that of the conventional silica-alumina catalysts and the products are virtually free of branched chain hydrocarbons. The divalent and trivalent metal exchanged forms of the sieve are much more active than NaX. Weisz and Miale ¹⁸⁰ found that the activity of the trivalent metal exchanged and hydrogen forms of synthetic fanjasites can exceed that of silica-alumina by factors greater than 10,000.

Pickert et al ¹⁷⁴ suggested that in the cracking of hexane carbonium ion~~s~~ intermediates were involved. The type X sieves were less active than the Y type and with the alkaline earth exchanged sieves greater activity was found with the smaller cations. The activity of various forms of zeolites for the cracking of n-hexane and cumene have been reported by Miale et

al¹⁸¹ and Topchieva et al¹⁸². Many other papers have been published on the catalytic cracking of hydrocarbons on zeolite catalysts. The authors generally agree that carbonium ion intermediates are involved although as was the case with silica-alumina catalyst the nature of the active site is a matter of controversy.

It is estimated that zeolite catalysts are currently employed in over 50% of the installed capacity of the oil refining industry⁴⁷. These catalysts consist of 5-15 wt.% of various multivalent metal cation and decationised forms of the molecular sieve zeolites in combination with other silica-alumina matrix materials and have many advantages over conventional cracking catalysts.

Olefin Polymerisation

Synthetic zeolites are also active for olefin polymerisation. Norton⁴¹ reported that the catalytic activity of 10X molecular sieve (CaX) was greater than that of NaX. The order of olefin re activities was reported to be 1-butene > propylene > ethylene and products were similar to those found for conventional acid catalysts. Activities for a series of ion exchanged molecular sieves for propylene and ethylene polymerisation have recently been reported by Nishizawa et al¹⁸³.

Aromatics Alkylation

Rare earth exchanged X and Y zeolites have been shown to

be versatile catalysts for the alkylation of aromatics. Mays et al.⁴⁰ reported that thiophene, thiophenol and phenolic ethers which are degraded in the presence of mineral acids are alkylated with good selectivity and high yields over zeolite catalysts. Venuto et al.⁴² studied the alkylation of simple monocyclic aromatic nuclei such as benzene, phenol and thiophene with a wide variety of alkylating agents. Operation in the liquid phase at temperatures of 150-230°C enabled efficient alkylation of simple aromatics with a variety of olefins, alcohols and haloalkanes to be carried out. Higher temperatures were required for dealkylation reactions, alkylations with paraffins and toluene disproportionation. In the alkylation of substituted benzenes, ortho: para orientation of substituents was observed.

Zeolites are more active for alkylation than silica-alumina catalysts¹⁸⁴ under comparable conditions. Their activity has been attributed to the presence of highly acidic sites which are capable of forming carbonium ions from reactant molecules⁴³.

Isomerisation

Multivalent metal cation and decationised catalysts prepared from type Y zeolites and containing about 0.5 wt.% of noble metal have been found to be highly active and selective for the isomerisation of C₄ to C₆ n-paraffins.^{46,174,169,185} n-Hexane can be isomerised on CaX at temperatures of 350°C. Ring position isomerisation of alkyl substituted benzenes are effected on multivalent metal cation exchanged and decationised

Y type zeolites in the temperature region $150 - 250^{\circ}\text{C}$ ^{184,47} and it has been suggested that transalkylation is the first step in the isomerisation reaction. Double bond isomerisation of i-butene has also been investigated on X type molecular sieves where the trivalent metal exchanged forms have shown high activity¹⁸³.

In addition to the above, molecular sieve zeolites, in their various forms have shown unusual properties in a variety of other catalytic reactions including hydrogenation, dehydrogenation, alcohol dehydration, dehalogenation, desulphurisation, condensation and oxidation reactions. Here the zeolite may function as the active catalysts or act as supports for most of the conventionally used metal or metal compound co-catalysts.⁴⁷

The high catalytic activity of molecular sieve zeolites has been ascribed to their open, three dimensional crystalline framework and the highly polar surface available within their uniform pore system. The evidence provided by the reactions which have been studied suggest that the monovalent metal cationic forms of X zeolites tend to promote radical-type reaction intermediates. Exchange of the monovalent for multivalent cations gives rise to carbonium-ion type activity which increases with increasing silica-alumina ratio of the zeolite and with the extent of multivalent cation exchange.¹⁸⁵ Carbonium-ion type activity is also imparted to the zeolite by decationization.

Several theories have been advanced to explain the very

high carbonium-ion type activity of these decationised and multi-valent metal exchanged forms of zeolite. Their activity in catalytic cracking ⁴⁵ olefin polymerisation ⁴¹ and aromatics alkylation ^{42,43} has been attributed by some workers to conventional Brønsted acid sites. These sites may be formed on the multi-valent metal cation forms by the formation of protons during the ionisation of strongly held water molecules at cation sites ⁴³. Evidence advanced to support this theory is provided by infra-red, deuterium exchange and thermogravimetric analyses which show residual water and surface-bound hydroxyl groups after dehydration at temperatures of 300-350°C ^{168,170,175,186,187}. Furthermore, Hirschler has shown that dehydrated zeolites react with triphenyl carbinol and other Hammett indicators to give the corresponding coloured carbonium ions, ¹⁸⁷, a property ascribed to the ability of the zeolite to release ⁵ protons.

Evidence has also been presented that decationised zeolites contain a large number of Lewis acid sites, attributed to the 3-co-ordinated aluminium atoms which are formed in the second step of the decationisation reaction ^{168,169,188}. Turkevich et al. ¹⁸⁹ have shown a parallel between the E.S.R. spectra (ascribed to Lewis acid sites) and catalytic activity in a number of reactions proceeding through carbonium ion type intermediates. Liengme and Hall ¹⁹⁰ have also shown that the I.R. spectra of pyridine adsorbed on a decationised zeolite is indicative of the presence of Lewis acid sites.

A third theory has been advanced to account for the unusually strong carbonium-ion type activity of the multi-valent cation and decationised forms of type X and type Y sieves by the ability of strong electrostatic fields at positive and negatively charged sites in the crystal lattice to form reactive semi ion-pair species by polarising hydrocarbon molecules ¹⁷⁴. This theory is based in part on crystallographic studies of the multi-valent metal cation zeolites and the relationships between the location of various cation sites and catalytic activity. This theory offers a plausible explanation of the observed similarity in the activity of the multi-valent metal cation and the decationised forms, despite significant differences in their chemical compositions.

Although three theories have been advanced concerning the mechanism of carbonium ion formation from hydrocarbons none of them have been accepted as being generally applicable. The concept of cation polarising power can explain the increase in catalytic activity with increasing cation charge and decreasing cation radius, but there are some facts which are hard to explain by this concept alone. The fact that the catalytic activity of zeolites decrease with increasing alumina content ¹⁶⁹ cannot easily be explained since the cation content parallels the alumina content. The supposition concerning a direct action of cations on the hydrocarbon molecules also makes it difficult to explain the promotion effect noticed on the

addition of small amounts of water to dehydrated zeolites ⁴², ¹⁹¹. The suggestion that acid sites due to casual defects or cation deficiency ¹⁹² are the active centres neither explains the difference in activity of the various cation forms nor the activity decreases with increasing alumina content. Also the report by Rabo et al. ¹⁷⁰ ^{that} the catalytic activity of CaY and CaX for cumene cracking is independent of the amount of OH groups present on the zeolite surface is contrary to the concept of the active site being in the form of a Brönsted acid, and the fact that the calcination temperature of alkali and alkaline earth Y sieves has to be greater than 500°C before Lewis acidity develops ¹⁹³ suggest that these sites may not be very important in reactions catalysed by these sieves.

Infra-red and other surface studies may help to resolve these problems. The present state of the knowledge gained from infra-red studies has been reviewed by Yates ¹⁹⁴. Although most of the work has been unsatisfactory due to experimental deficiencies, some pointers as to the location of OH groups and adsorbed species have been obtained. More work is required before the anomalies apparent at present are resolved.

The present work was undertaken in an attempt to find out about the nature of the catalytic action of these zeolites for the exchange reactions of hydrocarbons. Comparison of these results with others obtained on metals and oxide catalysts could yield valuable information concerning the nature of the catalytic

activity. Originally it was proposed to study the exchange of alkylbenzenes with deuterium but due to the zeolites difficulty in activating deuterium and the poor initial resolution of the mass spectrometer used for analysis most of the work was concerned with an examination of the catalytic activity of several ion exchanged forms of zeolite for the hydrogen/deuterium exchange reaction and for the exchange between low molecular weight hydrocarbons and heavy water.

CHAPTER 2

Experimental2.1 Preparation of Ion Exchanged Zeolites

The starting material used for ion exchange was the 13X sieve obtained from the Linde Division of the Union Carbide Corporation via B.D.H. Ltd. This sample was obtained in powder form, free of clay binder. The bulk sample from which various ion exchanged zeolites were prepared was analysed to show

$$\frac{\text{wt of silicon}}{\text{wt of aluminium}} = 1.27 \pm 0.02$$

The CaX, CoX, NiX and CuX sieves were prepared from one bulk sample of NaX; the MnX, ZnX, CeX, LaX and ThX were prepared from another bulk sample of NaX ¹⁹⁵ having the same silicon to aluminium ratio.

The exchange of sodium for other cations in NaX is simple and rapid. The speed of the exchange process is due in a large measure to the small crystal size of the zeolite particles (typically $0.1\text{--}2\mu$). The technique used to prepare the first series of sieves (CaX, CoX, NiX, CuX) was as follows.

A weighed amount of hydrated NaX, (about 10g), which had been stored over a saturated solution of $\text{Ca}(\text{NO}_3)_2$ to maintain a constant known degree of hydration, was slurried with 50ml. de-ionised distilled water in a 250ml. conical flask and evacuated by means of a water pump to expel air. The desired amount of exchange solution was then added to the slurry and the

volume made up to about 150ml. The flask was again evacuated to expel air from the solution and the mixture was kept for 12 hours at room temperature under vacuum. After exchange the solid was separated by decantation and filtered through a sintered glass crucible (porosity no.4). The solid was washed free of filtrate and the filtrate and washing made up accurately to 250mls. with distilled water. The filtrate was analysed quantitatively for amount of residual cation and the degree of exchange calculated as in the following example.

amount of hydrated NaX taken for exchange = X gms

exchange solution added to NaX slurry = Y gms metal

filtrate solution after exchange = Z gms metal

∴ amount of metal introduced into sieve = (Y - Z) gms

(Y - Z) gms metal ion replace $\frac{23 \times V \times (Y-Z)}{A}$ gms Na⁺

where A = atomic wt. and V = valence of exchange cation

∴ final wt. of exchanged sieve = $X + [Y-Z] - \left[\frac{23 \times V \times (Y-Z)}{A} \right]$
(assuming same degree of hydration as NaX) = B

∴ % metal ion content in sieve (hydrated) = $100 \left(\frac{Y-Z}{B} \right)$

composition of NaX ($\frac{Si}{Al} = 1.23$) = Na₈₆ [AlO₂ 86 SiO₂ 106] 264H₂O
(hydrated unit cell)

∴ 18164 gms hydrated NaX contain 1978 gms Na⁺

∴ % of Na⁺ replaced
(% exchange) = $\frac{100 \times 23 \times V \times (Y-Z) \times 18164}{A \times 1978 \times X}$

Analyses of original exchange solutions and filtrate solutions were carried out titrimetrically using a standardised E.D.T.A. solution as titrant. The indicators used for the various metals were as follows

estimation of Ca^{++}	- Eriochrome Black T
Co^{++}	- NaCl screened Methyl Thymol Blue
Ni^{++}	- NaCl screened Murexide

Estimation of Cu^{++} solutions were carried out by electrolysis.

The analyses of the other ion exchanged sieves (MnX , ZnX , CeX , LaX , ThX) were carried out in a different manner. The percentage exchange in these samples was obtained from measurements of the sodium contents of the ion exchanged forms using flame photometric methods 195.

In connection with ion exchange two general points should be made:

- 1) Any cation apart from the desired one should be rigorously excluded from the exchange solution (including ammonium ions) as the catalytically active ions may be very few in number.
- 2) The exchange solution should be alkaline if possible. In no case should the pH of the exchange solution be below pH5 since this may cause hydrolysis of the zeolite with consequent loss of structure and surface area.

The ion exchanged zeolites used in the present work are given in Table 2.1 together with the salt used for exchange and

Table 2.1 Ion-exchanged zeolites used as catalysts

Cation	% Exchange	exchange solution
Na ⁺⁺	100	-
Ca ⁺⁺	59	Ca(NO ₃) ₂
*Mn ⁺⁺	79	Mn Cl ₂ .6H ₂ O
Co ⁺⁺	9	Co(NO ₃) ₂ . 6H ₂ O
Co ⁺⁺	36	"
Co ⁺⁺	52	"
†Ni ⁺⁺	21	Ni(NO ₃) ₂ . 6H ₂ O
†Ni ⁺⁺	41	"
†Ni ⁺⁺	68	"
Cu ⁺⁺	9	CuSO ₄ .5H ₂ O
Cu ⁺⁺	37	"
Cu ⁺⁺	62	"
Cu ⁺⁺	69	"
Cu ⁺⁺	80	"
*Zn ⁺⁺	90	Zn SO ₄ .7H ₂ O
*Ce ⁺⁺⁺	24	Ce(NO ₃) ₃ .6H ₂ O
	86	"
*La ⁺⁺⁺	88	LaCl ₃ .7H ₂ O
*Th ⁴⁺	~10	Th(NO ₃) ₄ .6H ₂ O

* Catalysts prepared by D.R. Walker 195

† Catalysts prepared by N.E. Cross 196

the percentage exchange achieved. The partially exchanged sieves were obtained by adding a limited amount of exchange solution to the NaX-water slurry. The pure NaX used in experiments was subjected to a similar treatment as the ion exchanged sieves only using deionised distilled water instead of a salt solution.

2.2 Materials

Deuterium (99.5%) was the same as that used in Part II of this thesis. It was obtained in small 'lecture bottles' from the Matheson Company and was purified by diffusion through a palladium thimble followed by two liquid nitrogen traps in series.

Hydrogen (99.95%) was also obtained from the Matheson Company and was purified in a manner similar to that used for deuterium.

Deuterium oxide (99.7%) was obtained in 25gm containers from Imperial Chemical Industries Limited, and was degassed by vacuum distillation before use.

m-Xylene (99.91%) was the same as that used in Part II of this thesis and was used without further purification.

Propylene (99%), Ethylene (99%), 1-Butene (99%) and Iso-Butene (99%) were obtained from the Matheson Company in small 'lecture bottles'. They were purified and degassed before use by vacuum distillation and repeated cycles of freezing, pumping and thawing.

Isobutane (99.97%) was obtained from the Chemical Standards Division of the N.P.L. and was used without further purification

2.3 Experimental procedure

The apparatus used for carrying out isotopic exchange experiments has been described in Part I Chapter 3 of this thesis. For exchange reactions on zeolites the amount of catalyst taken was usually about 0.1gm. The activation procedure normally consisted of heating the catalyst under high vacuum. During the first two hours of evacuation the temperature of the catalyst in the reaction vessel was raised from room temperature to 400°C. This slow initial rate of heating was found necessary to prevent the catalyst particles from becoming 'fluidised' and streaming out of the reaction vessel. Also it was believed desirable to prevent contact between the water being desorbed and the catalyst at high temperatures, since it has been shown that water vapour under certain conditions can cause structural collapse of the zeolite crystals. After the temperature had reached $400 \pm 2^\circ\text{C}$ the temperature of the furnace surrounding the reaction vessel was stabilised by means of a 'Bikini' controller and the outgassing was continued for a further 10 hours, the dynamic pressure above the catalyst being about 10^{-6} torr.

After cooling the catalyst under vacuum, the desired reaction mixture was introduced and the temperature raised until reaction occurred. In the hydrogen/deuterium exchange

experiments the standard mixture of reactants consisted of equal parts of hydrogen and deuterium. The total pressure in the reaction vessel was 2.71cms. equivalent to 1.52×10^{20} molecules of hydrogen plus deuterium. In the exchange experiments between hydrocarbons and D_2O the amount of reactants were reduced to a minimum to ensure that diffusion effects were not operative. Usually a 1:2 mixture of hydrocarbon to D_2O was used, giving a total concentration of about 1.5 molecules per a cage of the catalyst, if they were both completely adsorbed. For 0.1gm catalyst this amounted to the equivalent of 4mm D_2O and 2mm hydrocarbon in the reaction vessel.

The reaction was monitored by allowing a very small continuous stream of gas to flow into the MS10 mass spectrometer through the capillary leak. Rate measurements were made at two or more temperatures during one run so that Arrhenius parameters could be calculated.

2.4 Mass Spectrometric Analyses

The energies of the ionising electrons used for the various molecules are given in Table 2.2. The voltages quoted were those, indicated on the electron beam control unit of the MS10, which gave the best compromise between fragmentation and sensitivity. Typical fragmentation patterns are also given.

The H_2/D_2 exchange experiments were carried out at 70 eV since the fragmentation of these molecules were small and there was no contribution from either molecule to the parent peak of

Table 2.2 Typical fragmentation patterns of hydrocarbons in the MS10 mass spectrometer

Molecule	electron volts	f ₁	f ₂	f ₃	f ₄	f ₅	f ₆	f ₇	f ₈	f ₉
ethylene	20	11	13							
ethane	20	55	368	18	9					
propylene	20	53	13	6						
propane	20	74	13	10	1					
isobutene	30	29	.5	7	2					
1-butene	30	35	9	11	8					
isobutane	70	107.5	22.5	19.0	2.5	22.5	6.5	31.5	37.5	9.0
m-xylene	20	32	3							

the reaction product molecule (i.e. HD). The experiments with isobutane were also carried out at 70 eV since the boost in sensitivity more than compensated for the loss of accuracy in calculating product distributions due to the increased fragmentation. The fragment peak at one mass unit lower than the parent was as large (relative to the parent peak) at 20 eV as it was at 70 eV. However, raising the electron voltage to 70 eV seemed to increase the proportions of the fragments caused by loss of more than one hydrogen atom.

Calculations of the fragmentation of the other isotopic

hydrocarbons were evaluated on a statistical basis which involved determining the chance of losing the appropriate number of hydrogen or deuterium atoms from the parent molecule assuming an equal chance for the loss of either atom. The methods have been illustrated previously in Part II of this thesis. The statistical weighting factors for propylene and ethane are the same as those for benzene; the factors for propane and the butenes are the same as those for toluene and the factors for isobutane are the same as those for m-xylene. The weighting factors for ethylene are given in table 2.3.

Table 2.3 Statistical weighting factors for fragmentation corrections for ethylene

Compound	mol. wt.	-1	-2	-3	-4
C_2D_4	32	0	f_1	0	f_2
$C_2H D_3$	31	$\frac{1}{4} f_1$	$\frac{3}{4} f_1$	$\frac{6}{12} f_2$	$\frac{6}{12} f_2$
$C_2H_2D_2$	30	$\frac{2}{4} f_1$	$\frac{2}{4} f_1 + \frac{4}{12} f_2$	$\frac{8}{12} f_2$	$\frac{2}{12} f_2 + \frac{12}{24} f_3$
C_2H_3D	29	$\frac{3}{4} f_1$	$\frac{1}{4} f_1 + \frac{5}{12} f_2$	$\frac{2}{4} f_2 + \frac{6}{24} f_3$	$\frac{3}{4} f_3$
C_2H_4	28	f_1	f_2	f_3	f_4

The isotope corrections used are given in Table 2.4. The changing contribution caused by the presence of naturally

occurring deuterium was usually ignored.

Table 2.4 Isotope corrections used for hydrocarbons.

Molecule	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	C ₄ H ₈	C ₄ H ₁₀	C ₈ H ₁₀
single isotope correction	2.2	2.3	3.3	3.4	4.4	4.5	8.8
double isotope correction	—	—	—	—	0.1	0.1	0.3

By use of the above isotope and fragmentation corrections the distribution of the various isotopic hydrocarbons at known times and temperatures were calculated from the observed peak heights of the mass spectrometer output and Arrhenius parameters calculated as described previously.

In the hydrogen-deuterium exchange experiments, rates were measured by application of the first order rate equation:

$$\log_{10} (HD_{\infty} - HD_t) = \frac{-kt}{2.303} + \log HD_{\infty}$$

where k is the rate constant for exchange and HD_{∞} and HD_t are the percentages of HD at equilibrium and at time t respectively, For the exchange of hydrocarbons with D_2O the equation used was that discussed on Page 24 (equation 5).

CHAPTER 3

Results

3.1 Nature of the Catalysts

X-ray Diffraction traces

An x-ray powder diffraction trace was taken for each sieve using a Philips x-ray diffractometer operated at 40 KV with a 20 M.A. beam and a copper target. Scans between $2\theta = 4^\circ$ and 35° were taken at a speed of $2^\circ/\text{min}$ and displayed on a chart recorder. For each sieve the (III) peak, occurring at $2\theta \approx 6^\circ$ was the major peak. Typical traces are shown in Figure 3.1. It was found that all the catalysts shown in Table 2.1 were of a crystalline nature except the CuX zeolite which was 80% exchanged. This sieve gave only a weak diffraction trace and it was concluded that the exchange process had caused the major portion of the structure to collapse. To test the stability of the zeolite under reaction conditions, the residues remaining after exchange reactions involving D_2 or D_2O had been carried out, were used to obtain diffraction traces. In no case, where such spectra were recorded, was structural collapse evident.

Thermogravimetric Analyses

Thermogravimetric analyses were carried out on samples of NaX, CaX and CoX to determine their water content. The apparatus used consisted of a torsion balance capable of reading up to 500 mg. from which the sample, contained in a

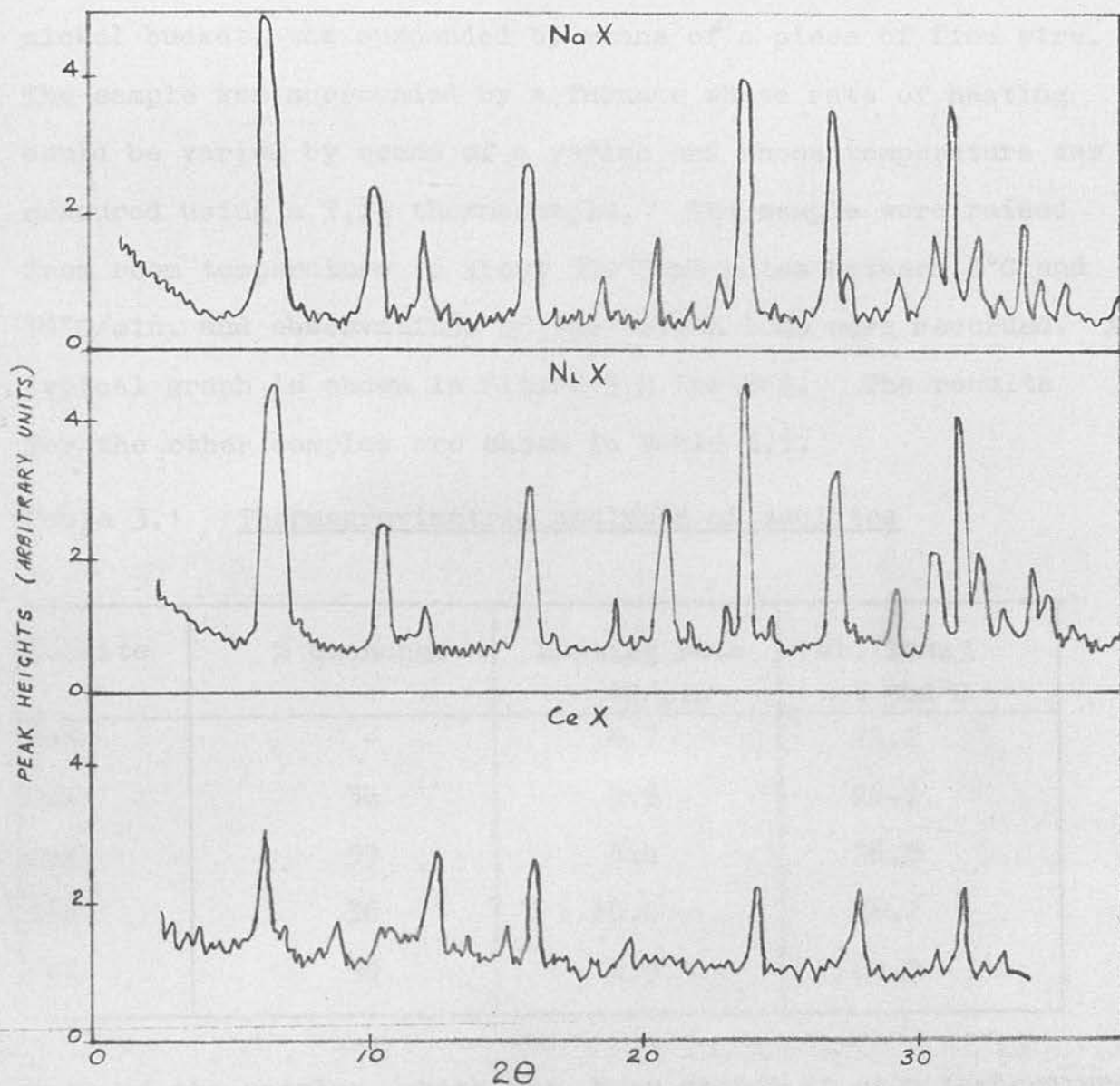


FIGURE 3.1

X-RAY DIFFRACTION TRACES FOR NaX, NLX and CeX ZEOLITES.
TRACES ARE FOR THE MOST HIGHLY EXCHANGED SAMPLES.

nickel bucket, was suspended by means of a piece of fine wire. The sample was surrounded by a furnace whose rate of heating could be varied by means of a variac and whose temperature was measured using a T_1T_2 thermocouple. The sample were raised from room temperature to about 500°C at rates between 8°C and $10^\circ\text{C}/\text{min.}$ and observations of the weight loss were recorded. A typical graph is shown in Figure 3.2 for NaX. The results for the other samples are shown in Table 3.1.

Table 3.1 Thermogravimetric analysis of zeolites

Zeolite	% exchange	heating rate $^\circ\text{C}/\text{min}$	wt. loss% at 500°C
NaX	-	8.7	25.2
CaX	34	9.5	26.2
CaX	59	8.4	26.0
CoX	36	10.0	26.2
CoX	52	8.3	27.0

Each of the samples, which had been stored at room temperature over a saturated solution of $\text{Ca}(\text{NO}_3)_2$ before analysis, gave the same percentage weight loss on heating to 500°C (within experimental error) and on cooling reverted to their original degree of hydrations demonstrating that their crystal structure had not been broken down.

One feature, which was common to all samples involved

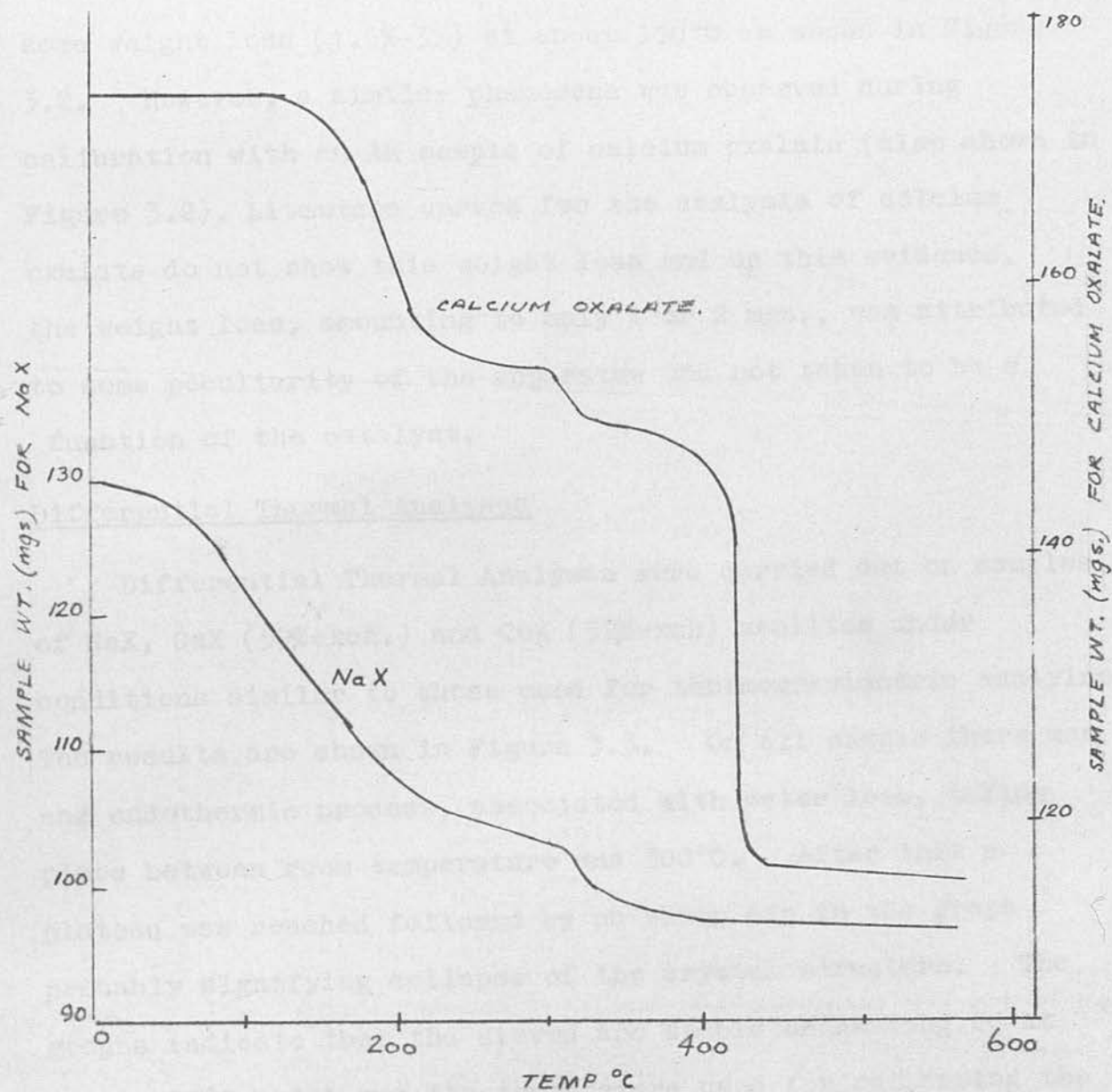


FIGURE 3.2.

THERMOGRAVIMETRIC ANALYSIS CURVES FOR NaX (HEATING RATE 8.7°C/min.) AND CALCIUM OXALATE (RATE 8.9°C/min.)

some weight loss (1.5%–3%) at about 350°C as shown in Figure 3.2. However, a similar phenomena was observed during calibration with an AR sample of calcium oxalate (also shown in Figure 3.2). Literature curves for the analysis of calcium oxalate do not show this weight loss and on this evidence, the weight loss, amounting to only 1 or 2 mgs., was attributed to some peculiarity of the apparatus and not taken to be a function of the catalyst.

Differential Thermal Analyses

Differential Thermal Analyses were carried out on samples of NaX, CaX (59%exch.) and CoX (52%exch) zeolites under conditions similar to those used for thermogravimetric analyses. The results are shown in Figure 3.3. On all sample there was an endothermic process, associated with water loss, taking place between room temperature and 300°C. After this a plateau was reached followed by an sharp dip in the graph probably signifying collapse of the crystal structure. The graphs indicate that the sieves are stable on heating to at least 400°C which was the temperature used for outgassing the catalysts prior to carrying out catalytic exchange reactions. CoX seems to be less stable to heat than either NaX or CaX.

Surface Areas

Surface area measurements (by nitrogen adsorption) on the zeolites used in this work have been carried out by other researchers in the Chemistry Department of the University of

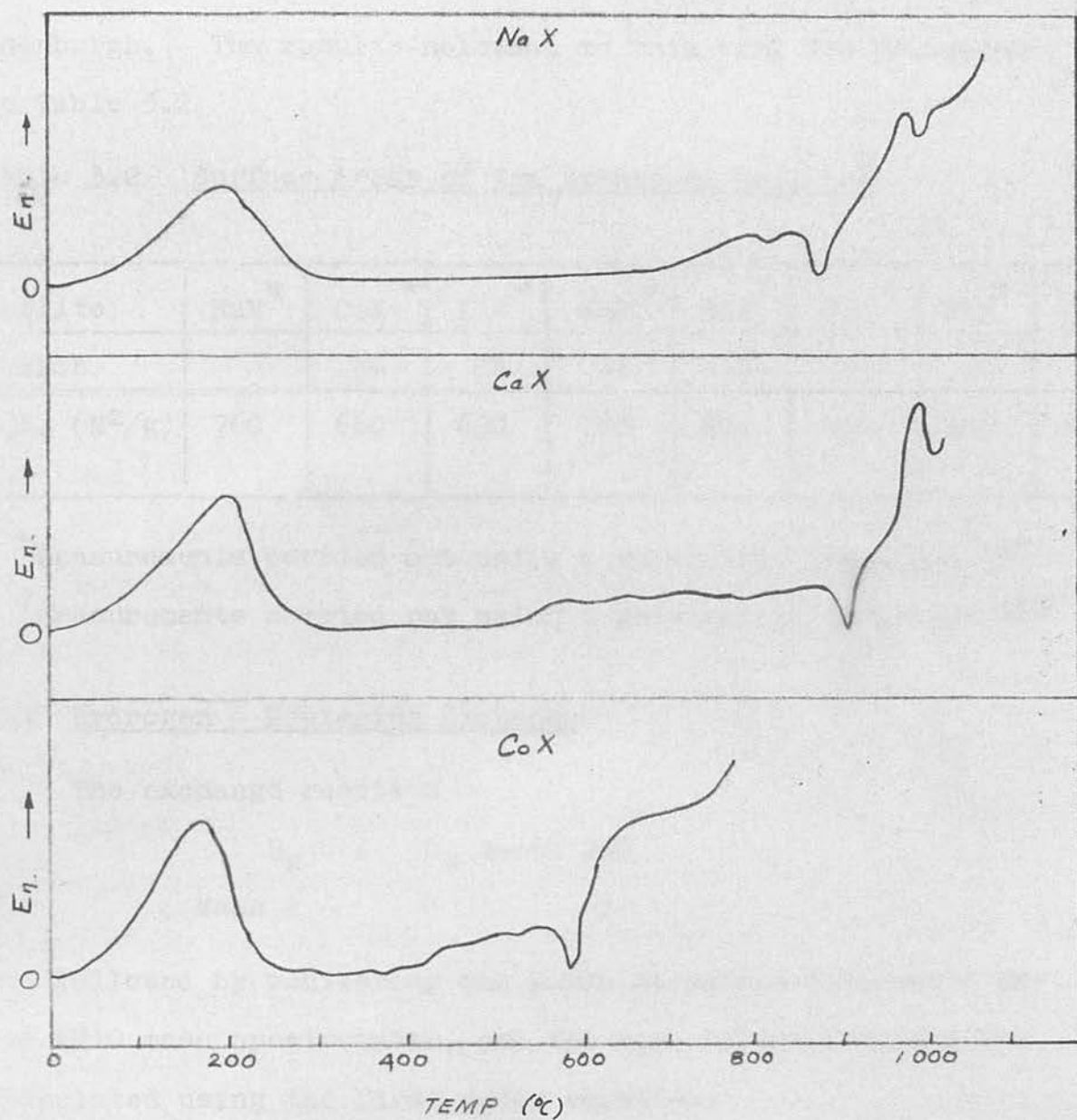


FIGURE 3.3

DIFFERENTIAL THERMAL ANALYSIS CURVES FOR ZEOLITES. E_n is ENDOTHERMIC. TEMP. GRADIENT $8.35^\circ\text{C}/\text{min.}$ CURVES ARE FOR MOST HIGHLY EXCHANGED SAMPLES.

Edinburgh. The results relevant to this work are presented in Table 3.2

Table 3.2 Surface Areas of Ion exchanged Zeolites

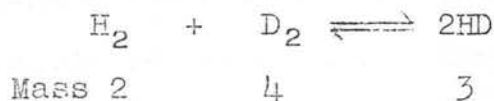
Zeolite	NaX [*]	CeX [*]	LaX [*]	MnX [*]	NiX [†]	NiX [†]	NiX [†]	CuX [†]
% exch.	--	86	68	86	68	41	21	62
S.A. (M ² /g)	760	660	690	780	894	850	890	818

* Measurements carried out using a volumetric technique 195

† Measurements carried out using a gravimetric technique 196

3.2 Hydrogen - Deuterium Exchange

The exchange reaction



was followed by monitoring the peaks at masses 2,3, and 4 on the MS10 mass spectrometer, and the rate of the reaction was calculated using the first order equation:

$$\log_{10} (\text{HD}_{\infty} - \text{HD}_t) = \frac{-kt}{2.303} + \log_{10} \text{HD}_{\infty}(1)$$

where k is the rate constant for exchange and HD_{∞} and HD_t are the percentages of HD at equilibrium and at time t respectively. HD_{∞} was calculated from the data of Urey and Rittenberg 197 and it was found that these values for the equilibrium constant of the reaction given by

$$K = \frac{[HD]^2}{[H_2][D_2]} \quad (2)$$

were similar to those calculated experimentally from an equilibrium mixture of isotopes assuming equal sensitivity for each component in the mass spectrometer, corrections for background being made but fragmentation ignored. The equilibrium constant above varies with temperature as shown in Figure 3.4 and from this graph the appropriate value of HD_{eq} for use in equation (1) was chosen to correspond with the temperature at which the exchange was being carried out. The rate of reaction was measured at two or more temperatures during one run so that Arrhenius parameters could be calculated.

The results obtained for a number of ion exchanged X sieves are given in Table 3.3. These results were corrected for reaction on the walls of the reaction vessel. This blank reaction occurred with an activation energy of 9.5 Kcal/mole and a reaction rate of 0.1%/min at 360°C with a 'pyrex' reaction vessel. When a silica reaction vessel was used much the same activation energy was found (9.4 Kcal/mole) but the activity was 32 times lower. The rate of reaction on CaX could not initially be separated from the rate of the blank reaction and it was assumed that under the conditions used for exchange this catalyst was inactive. The pre-exponential factors ($\log_{10}A$) in Table 3.3 are given in molecules/sec 0.1 gm of hydrated sieve.

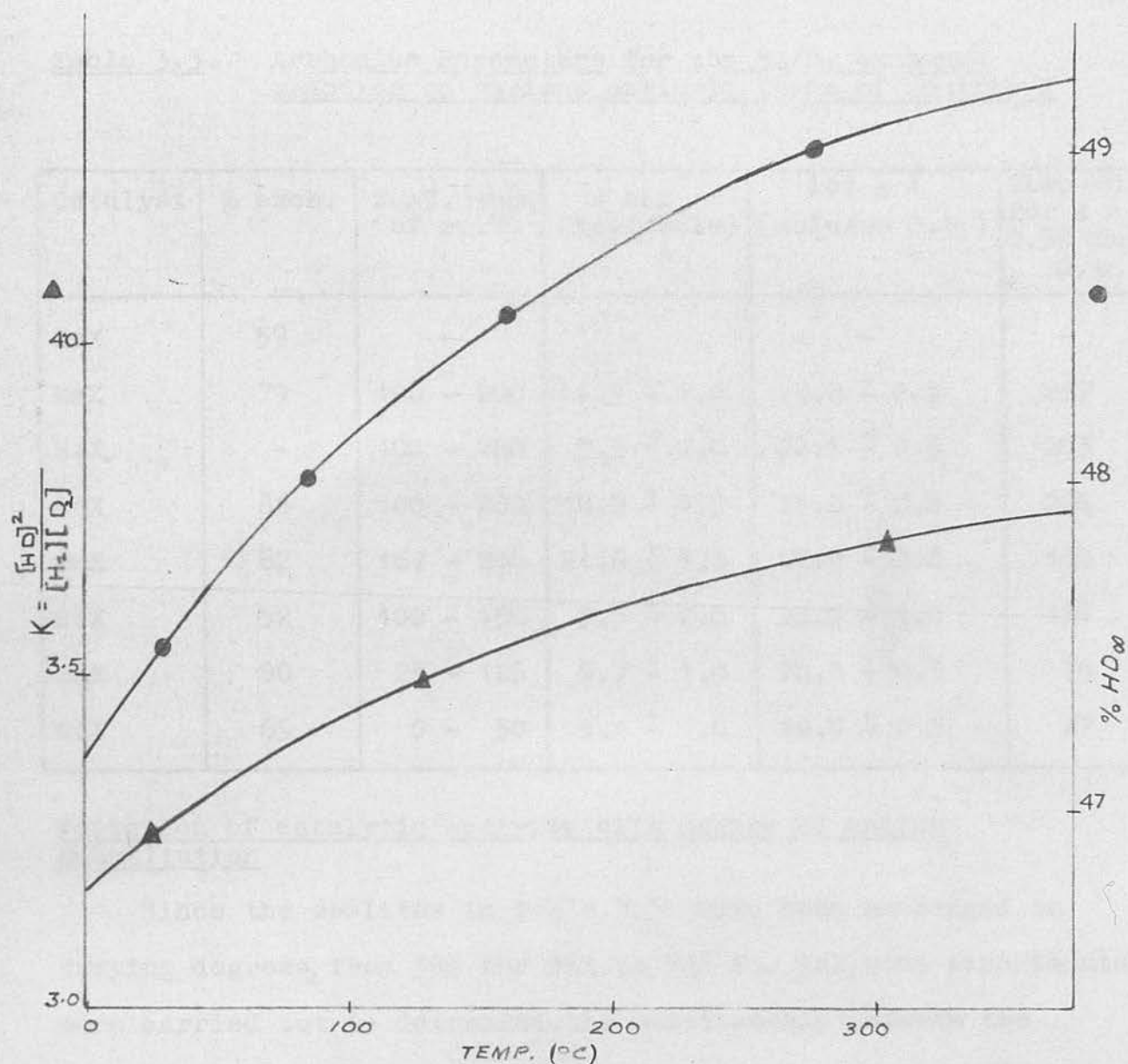


FIGURE 3.4

VARIATION OF THE EQUILIBRIUM BETWEEN H_2 , HD and D_2 WITH TEMPERATURE. % HD $_{\infty}$ IS THE CALCULATED EQUILIBRIUM PERCENTAGE OF HD FOR GAS MIXTURES CONTAINING EQUAL AMOUNTS OF HYDROGEN AND DEUTERIUM.

Table 3.3. Arrhenius Parameters for the H_2/D_2 exchange reaction on various cationic forms of zeolite X

Catalyst	% exch.	Temp. range of rxn. °C	E act (Kcal/mole)	$\log_{10} A$ (mole/sec 0.1g)	Temp °C for $k = -1$ $0.5\% \text{ min}^{-1}$ $0.1g.$
CaX	59	-	-	-	-
MnX	79	100 - 200	11.1 ± 1.0	17.0 ± 0.5	257
NaX	-	100 - 240	9.3 ± 1.0	22.1 ± 0.5	203
CeX	86	100 - 200	14.9 ± 1.5	25.3 ± 0.8	224
CuX	62	167 - 204	21.6 ± 1.5	28.6 ± 0.8	160
CoX	52	100 - 150	9.5 ± 2.0	23.2 ± 1.0	135
ZnX	90	25 - 125	9.7 ± 1.0	24.2 ± 0.5	75
NiX	65	0 - 50	5.1 ± 1.0	22.9 ± 0.5	27

Variation of catalytic activity with degree of cation substitution

Since the zeolites in Table 3.3. have been exchanged to varying degrees, from 59% for CaX to 90% for ZnX, some experiments were carried out to determine the relationship between the degree of exchange and the catalytic activity for the hydrogen-deuterium exchange reaction. These experiments were carried out on the cobalt exchanged forms. The results are presented in Table 3.4.

These results show that the exchange activity increases with the amount of Co^{++} ions present in the sieve although there is not a linear relationship, the greatest difference occurring between catalysts of low cobalt ion content.

Table 3.4. Effect of degree of cation substitution on the catalyst activity for H_2/D_2 exchange

Catalyst	% exch.	Temp range of rn. °C	E act (Kcal/mole)	Log ₁₀ A (mole/sec 0.1g)	Temp °C for k = 0.2 %/ min 0.1g
NaX	0	100 - 240	9.3 ± 1.0	22.1 ± 0.5	170
CoX	9	100 - 150	9.5 ± 2.0	22.9 ± 1.0	132
CoX	36	100 - 150	9.5 ± 2.0	23.0 ± 1.0	119
CoX	52	100 - 150	9.5 ± 2.0	23.2 ± 1.0	105

Variation of catalytic activity with temperature of outgassing

A series of experiments was also conducted, using the 36% exchanged CoX sieve, to determine the effect of outgassing temperature on the catalytic activity. As the outgassing temperature is increased the amount of residual water on the catalyst surface will decrease and this may have an effect on the exchange reaction. The results, presented in Table 3.5., show that the catalytic activity is increased on raising the outgassing temperature from 197°C to 395°C.

Table 3.5. Effect of outgassing temperature on the H_2/D_2 exchange activity of CoX (36% exch.)

Temp. of outgassing (°C)	Temp range of rn. °C	E act (Kcal/mole)	Log ₁₀ A (mole/sec 0.1 g)	Temp for k = 0.1%/ min 0.1g.
197	100 - 190	11.6 ± 2.0	23.7 ± 1.0	129
296	100 - 125	9.5 ± 2.0	22.6 ± 1.0	130
395	100 - 150	9.5 ± 2.0	23.0 ± 1.0	99

There was one noticeable difference between the catalyst outgassed at 197°C and those outgassed at 296°C and 395°C, apart from the differences in Arrhenius parameters. On the catalyst outgassed at 197°C there was another reaction occurring which resulted in an increase in the amount of 'H' isotope in the gas phase 'hydrogen'. In one run the initial gas mixture admitted to the catalyst contained almost equal parts H₂ and D₂, the 'H' content being 48.6%. It was found that this value increased on reaction at 143°C and after 20 hours at 185°C had reached an equilibrium value of 58.4%. This process, which was attributed to the presence of a subsidiary reaction, obeyed first order kinetics and Figure 3.5. shows the rate plots obtained for this process using the first-order rate equation:

$$\log_{10} (H_{\infty} - H_t) = \frac{-kt}{2.303} + \text{constant} \quad (3)$$

where H_t and H_∞ are the percentages of H isotopes at time t and at equilibrium respectively. The slopes of the lines gave rates, in %/min 0.1g, which corresponded closely to those obtained for the H₂/D₂ exchange reaction at the same temperatures as is shown by the Arrhenius plots for these two reactions (Figure 3.6.).

In the calculation of the rates for H₂/D₂ exchange the effect of the changing ratio of 'H' to 'D' on HD_∞ (equation (1)) was ignored. This could be done without the introduction of

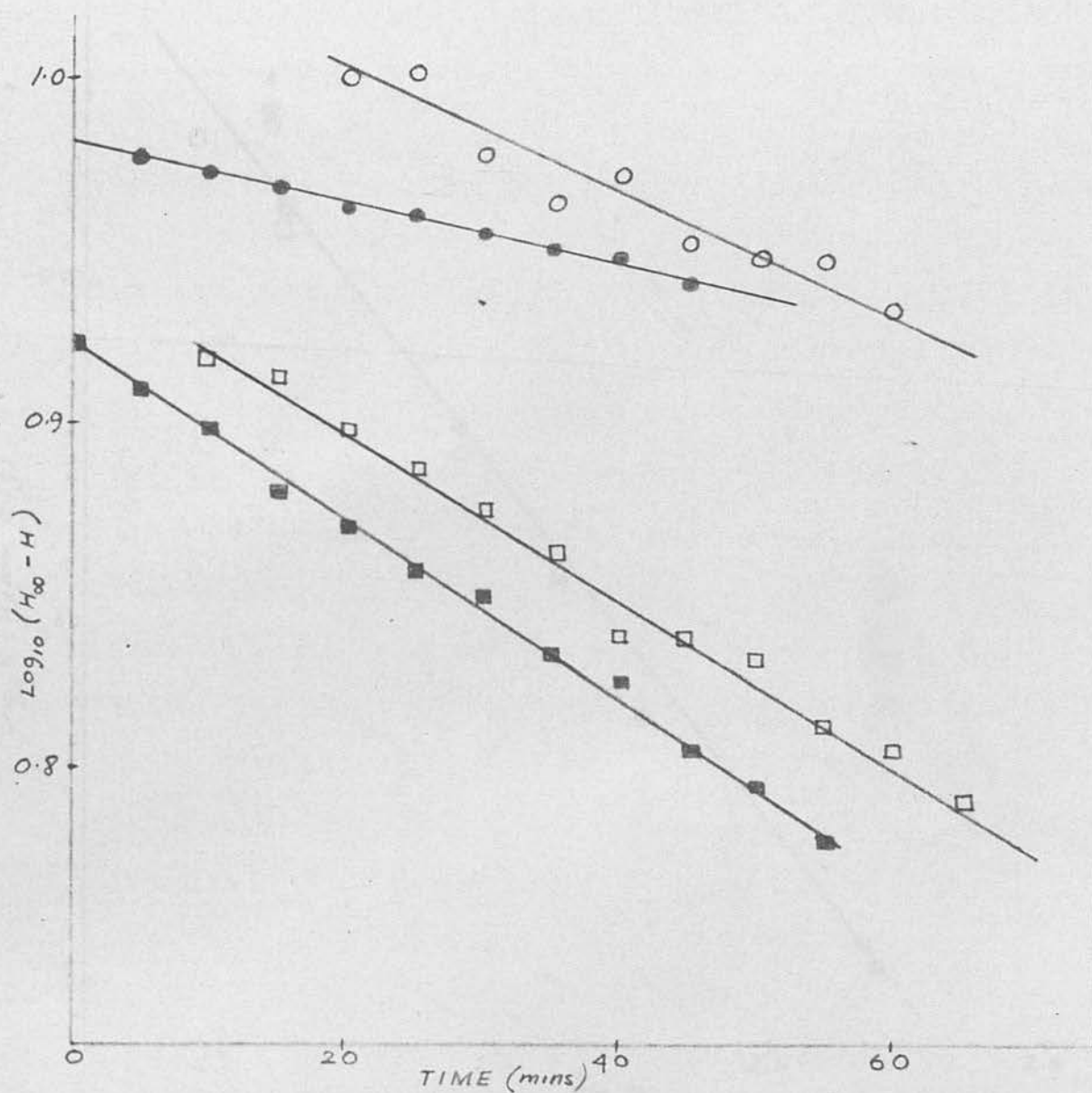


FIGURE 3.5

RATE PLOTS ACCORDING TO EQUATION (3) FOR THE DILUTION OF DEUTERIUM IN THE ISOTOPIC 'HYDROGENS' FROM TWO EXPERIMENTS. ● & ■ REACTION ON CoX (36% EXCH.) AT 148°C & 173°C RESPECTIVELY (RUN 1). ○ & □ REACTION ON CoX (36% EXCH.) AT 172°C & 186°C RESPECTIVELY (RUN 2).

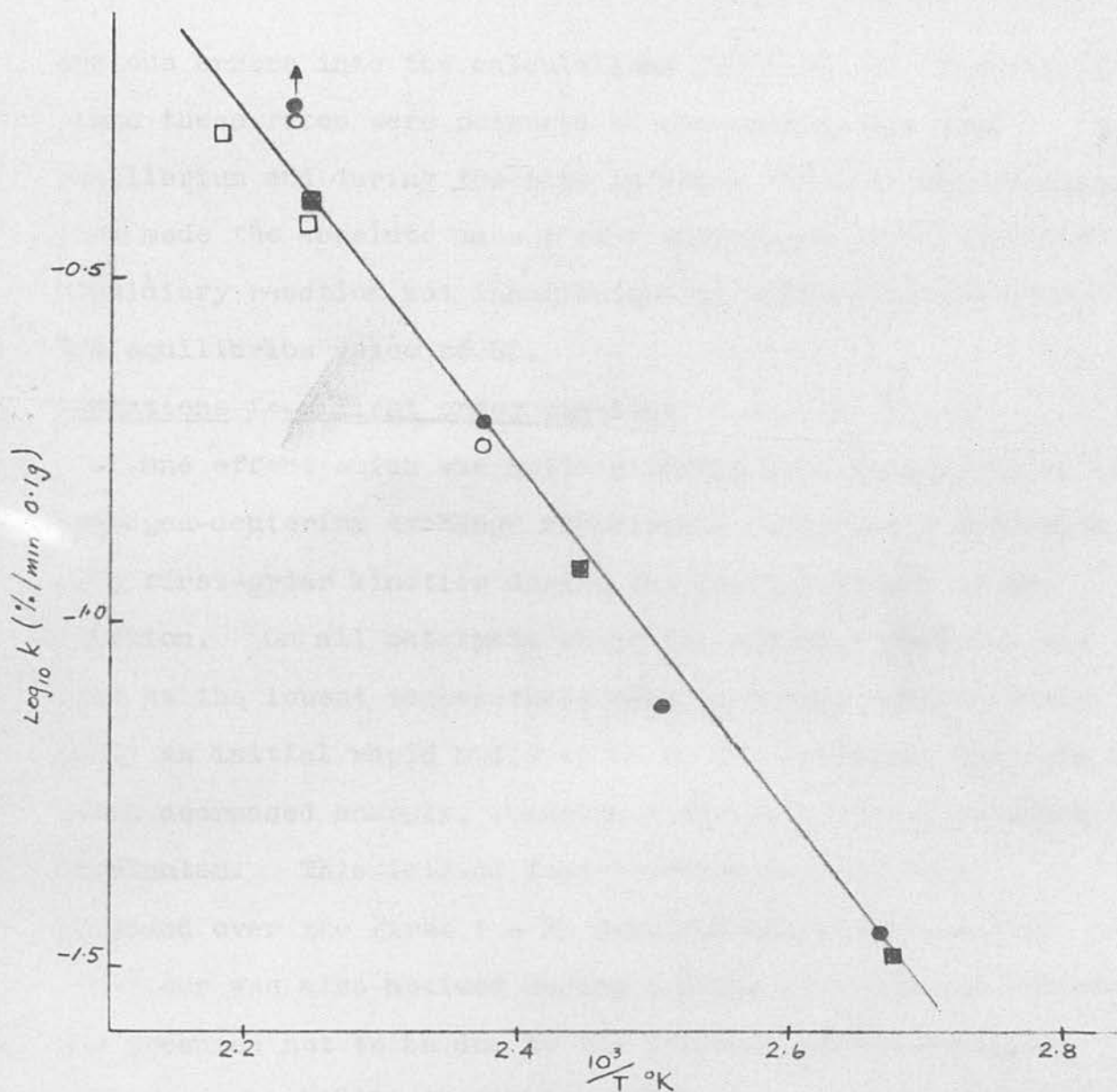


FIGURE 3.6.

ARRHENIUS PLOTS FOR THE HYDROGEN/DEUTERIUM AND
'DEUTERIUM DILUTION' REACTIONS ON CoX (36% EXCH.)
OUTGASSED AT 197°C

●, ■ RATE OF INCREASE OF % HD

○, □ RATE OF INCREASE OF % H

○, ● RUN 1 ; □, ■ RUN 2

serious errors into the calculations for the rate of exchange, since these rates were measured at conversions far from equilibrium and during the time in which the rate measurements were made the absolute amount of H enrichment caused by this subsidiary reaction was insufficient to alter significantly the equilibrium value of HD.

Deviations from first order kinetics

One effect which was noticed during practically all of the hydrogen-deuterium exchange experiments concerned a deviation from first-order kinetics during the initial stages of the reaction. On all catalysts where the exchange reaction was slow at the lowest temperatures used to measure rates (Table 3.3.) an initial rapid build up of HD was detected, the rate of which decreased sharply, reaching a steady state after about 15 minutes. This initial fast reaction however, only extended over the first 1 - 2% reaction and since the same behaviour was also noticed during a blank reaction the effect was presumed not to be due to the presence of the catalyst. It seems more likely that this effect was caused by exchange on the glass walls of the reaction vessel, the initial high activity rapidly being lost, presumably due to poisoning. Figure 3.7. shows the type of initial rate plots obtained in the presence of a catalyst and in the blank reaction. In all cases the steady state rate was taken to be the true reaction rate and only these rates were used in the calculation of

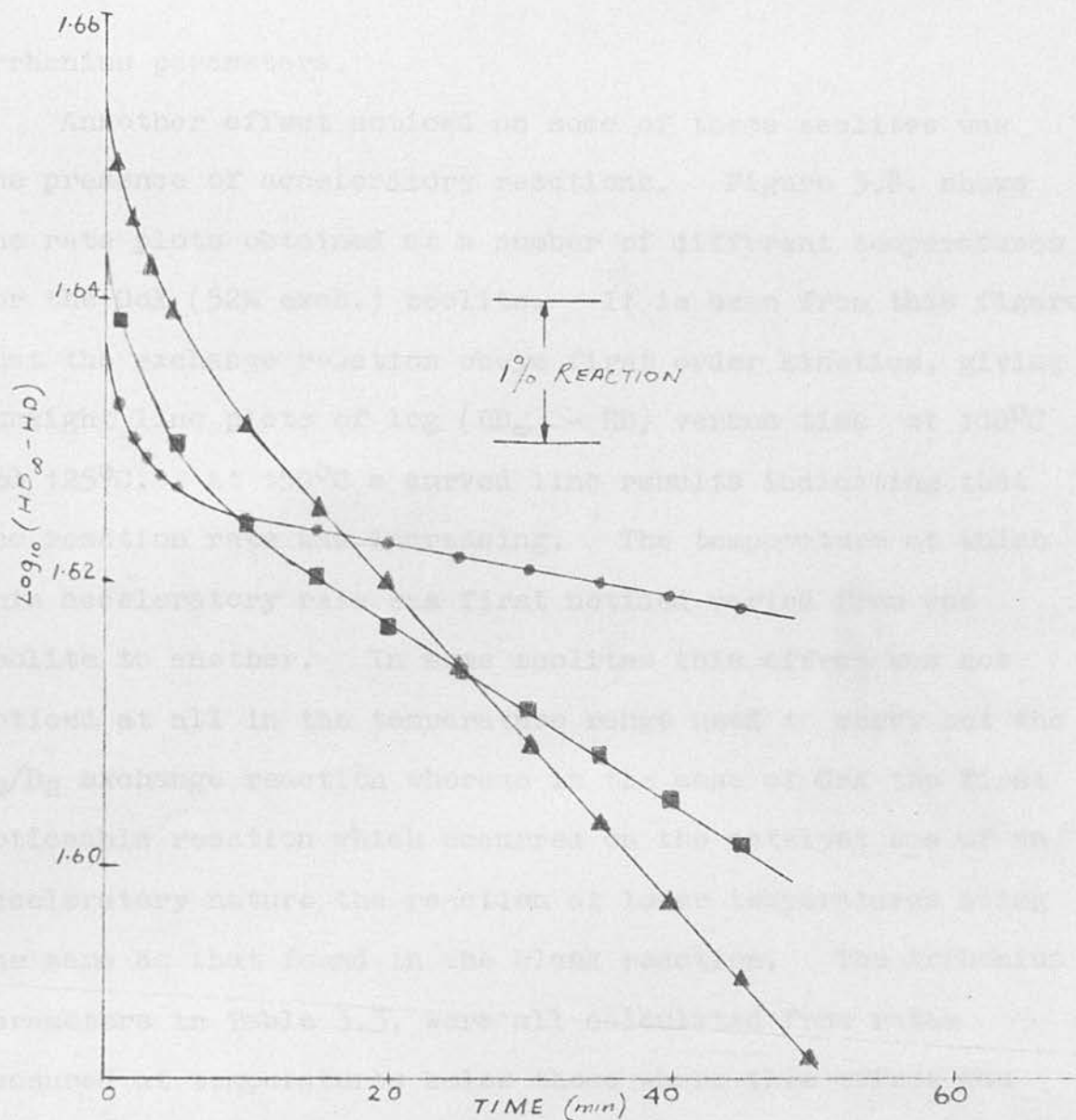


FIGURE 3.7

INITIAL RATE PLOTS FOR THE H_2/D_2 EXCHANGE REACTION

- \bullet BLANK REACTION AT 103°C
- \blacktriangle REACTION ON CoX (52% EXCH.) AT 100°C
- \blacksquare REACTION ON ZnX (90% EXCH.) AT 24°C

Arrhenius parameters.

Another effect noticed on some of these zeolites was the presence of acceleratory reactions. Figure 3.8. shows the rate plots obtained at a number of different temperatures for the CoX (52% exch.) zeolite. It is seen from this figure that the exchange reaction obeys first order kinetics, giving straight line plots of $\log (HD_{\infty} - HD)$ versus time at 100°C and 125°C. At 150°C a curved line results indicating that the reaction rate was increasing. The temperature at which this acceleratory rate was first noticed varied from one zeolite to another. In some zeolites this effect was not noticed at all in the temperature range used to carry out the H_2/D_2 exchange reaction whereas in the case of CaX the first noticeable reaction which occurred on the catalyst was of an acceleratory nature, the reaction at lower temperatures being the same as that found in the blank reaction. The Arrhenius parameters in Table 3.3. were all calculated from rates measured at temperatures below those where this effect was noticed.

Where this acceleratory reaction was evident the activities of the catalysts were also measured after pre-treatment with 'hydrogen'. After a normal run had been carried out, up to the temperature at which the reaction started to accelerate, the temperature of the reaction vessel was raised to about 50°C above this threshold temperature and

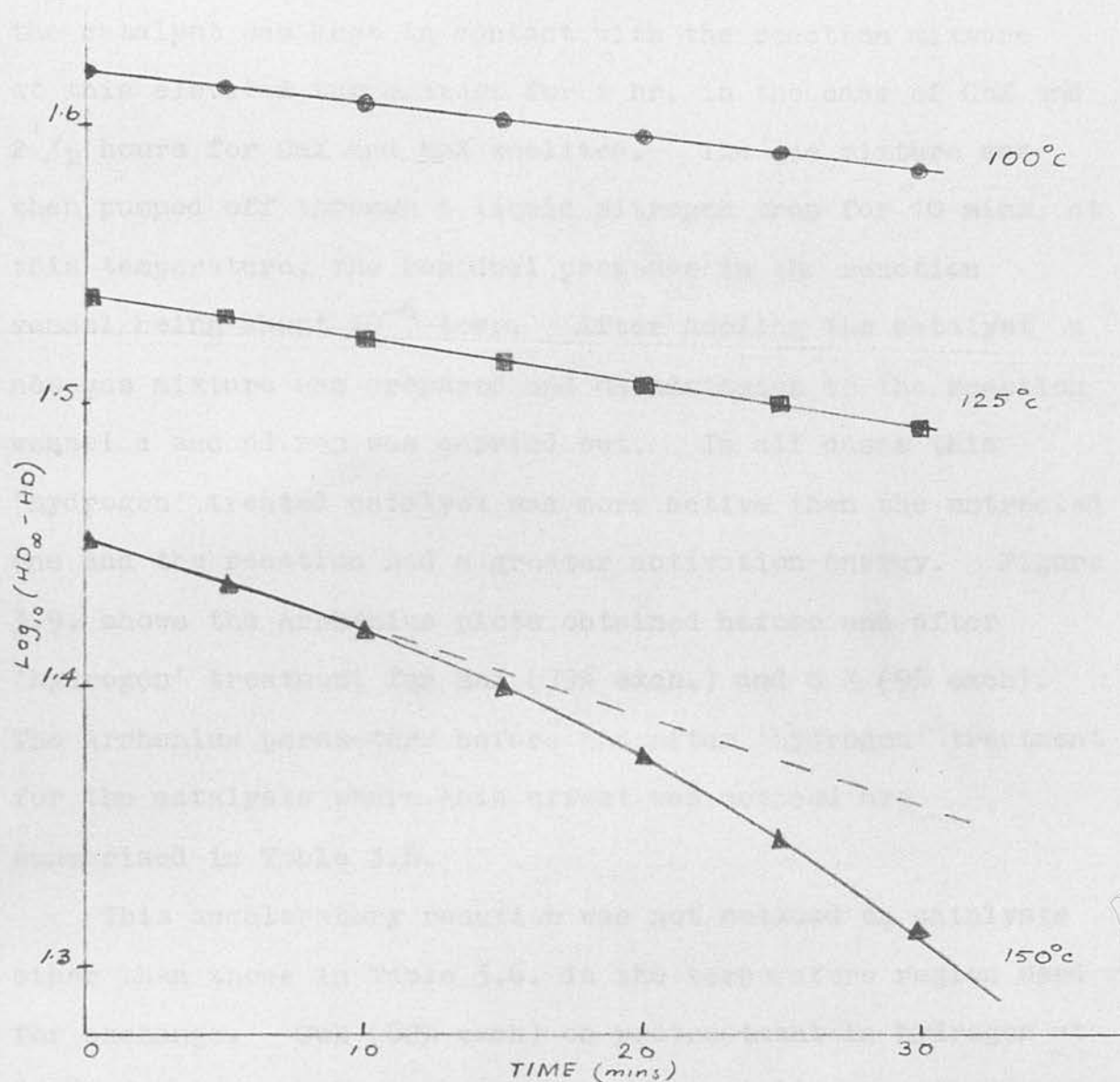


FIGURE 3.8

RATE PLOTS ACCORDING TO EQUATION (1) FOR THE EXCHANGE OF HYDROGEN WITH DEUTERIUM ON 0.1g C_6X (52% EXCH.) SHOWING ACCELERATING REACTION AT 150°C.

the catalyst was kept in contact with the reaction mixture at this elevated temperature for 1 hr. in the case of CoX and $2\frac{1}{2}$ hours for CaX and MnX zeolites. The gas mixture was then pumped off through a liquid nitrogen trap for 10 mins. at this temperature, the residual pressure in the reaction vessel being about 10^{-6} torr. After cooling the catalyst a new gas mixture was prepared and on admission to the reaction vessel a second run was carried out. In all cases this 'hydrogen' treated catalyst was more active than the untreated one and the reaction had a greater activation energy. Figure 3.9. shows the Arrhenius plots obtained before and after 'hydrogen' treatment for MnX (79% exch.) and CoX (9% exch.). The Arrhenius parameters before and after 'hydrogen' treatment for the catalysts where this effect was noticed are summarised in Table 3.6.

This acceleratory reaction was not noticed on catalysts other than those in Table 3.6. in the temperature region used for exchange. CuX (62% exch) on pretreatment in hydrogen at 300°C for 2 hours gave no increase in activity over the untreated catalyst. This Arrhenius plot is also shown in Figure 3.9. for the sake of comparison. There is another point to note here in connection with the results obtained on CoX outgassed at different temperatures. The catalyst outgassed at 197°C did not show this acceleratory reaction at 150°C and only very slightly at 173°C, the rate of exchange

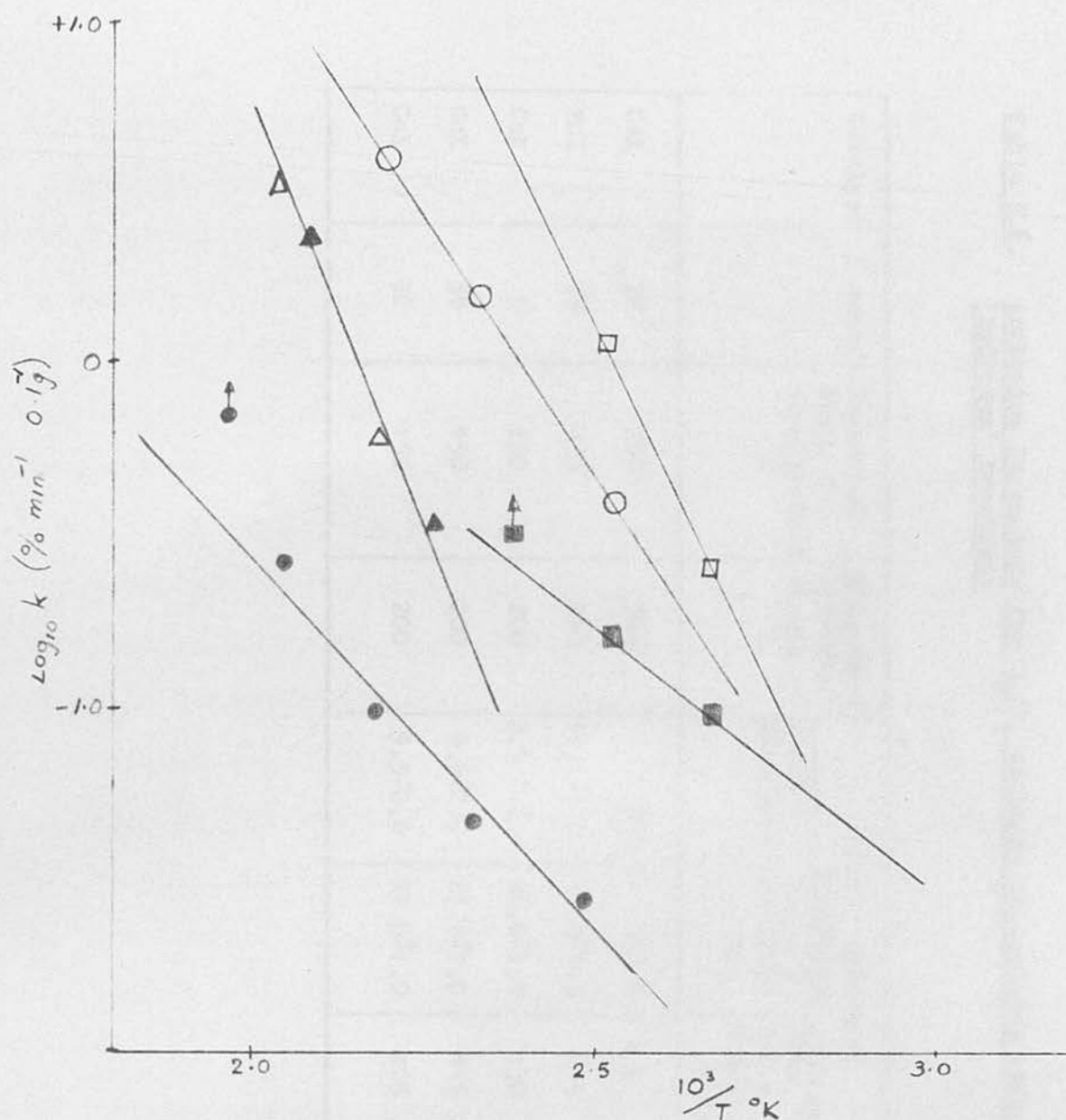


FIGURE 3.9

ARRHENIUS PLOTS FOR H_2/O_2 EXCHANGE ON ZEOLITES.

●	REACTION ON	M_nX (79% EXCH.)	BEFORE HYDROGEN TREATMENT				
○	"	"	"	AFTER	"	"	AT 290°C
■	"	"	C_6X (9% EXCH.)	BEFORE	"	"	
□	"	"	"	AFTER	"	"	AT 200°C
▲	"	"	C_6X (62% EXCH.)	BEFORE	"	"	
△	"	"	"	AFTER	"	"	AT 300°C

Table 3.6. Arrhenius Parameters for H₂/D₂ exchange on zeolites before and after 'hydrogen' treatment

Catalyst	% exch.	Threshold temp. for acceleration °C	Temp of 'hydrogen' treatment °C	Before 'hydrogen' treatment			After 'hydrogen' treatment				
				E act Kcal/mole	Log ₁₀ A mole ² /sec 0.1g.	Temp °C for k = -1 0.2/min ⁻¹ 0.1g.	E act Kcal/mole	Log ₁₀ A mole/sec 0.1g.	Temp °C for k = -1 0.2min ⁻¹ 0.1g.		
CaX	59	230	300	N O T A C T I V E							
Max	79	235	290			11.1 [±] 1.0	17.0 [±] 0.5	212	13.9 [±] 1.0	25.7 [±] 0.5	107
CoX	9	150	200			9.5 [±] 2.0	22.9 [±] 1.0	132	17.4 [±] 2.0	28.1 [±] 1.0	97
CoX	36	150	200			9.5 [±] 2.0	23.0 [±] 1.0	119	12.5 [±] 2.0	25.7 [±] 1.0	67
CoX	52	150	200			9.5 [±] 2.0	23.2 [±] 1.0	105	13.3 [±] 2.0	28.0 [±] 1.0	39

increasing by a factor of 1.25 in 30 mins. The catalyst outgassed at 296°C however, gave a very pronounced acceleratory reaction at 148°C, the rate increasing by a factor of 5 in 30 mins. This was even more pronounced than that found at 150°C with the catalyst outgassed at 395°C where a rate increase by a factor of 1.5 in 30 min. was found. The catalyst outgassed at 296°C had an initial activity for the exchange reaction which was 2.6 times lower than that for the catalyst outgassed at 395°C but on hydrogen treatment at 200°C for 2 hours and evacuation at this temperature for a further 2 hours the new activity was about twice that found with the catalyst initially evacuated at 395°C which had been hydrogen treated at 200°C for 1 hour and evacuated for 10 minutes.

Variation in Activity

Another anomalous feature of these zeolites was noticed during exchange experiments on different samples of CuX and NiX zeolites. With CuX zeolites the activities of a number of different preparations were tested for the hydrogen-deuterium exchange reaction. It was found that there were large differences in activity between samples containing similar amounts of copper ions. The Arrhenius parameters for two of these samples are given in Table 3.7. Both of these samples were prepared from the same bulk sample of NaX and copper sulphate (pH = 3.8). Sample I was prepared by ion exchange for three hours at room temperature with a saturated

solution of copper sulphate. Sample II was prepared by ion exchange for $2\frac{1}{2}$ hours at room temperature with a solution containing $10\text{g Cu}^{++}/\text{litre}$.

Table 3.7. Arrhenius parameters for H_2/D_2 exchange on two different preparations of CuX

Sample No	I	II
% exch.	?	62
Temp. range of run $^{\circ}\text{C}$	0 - 25	167 - 204
E act (Kcal/mole)	3.0 ± 1.0	21.6
$\text{Log}_{10} A$ (mol./sec 0.1g)	21.5 ± 0.5	28.6
Temp $^{\circ}\text{C}$ for $k =$ 50%/min 0.1g.	-5°C	224

The amount of Na^+ replaced by Cu^{++} in sample I was not measured since only a small amount of catalyst was prepared. However, it is unlikely that the amount of exchange was greater than 70% since the colour of the sample (torquoise blue) was very similar to that of a 69% exchanged sieve and much paler than an 30% exchanged sieve. Both the 69% and the 80% exchanged sieves which had been prepared respectively by exchanging for 12 hours using the same materials as for sample II and by repeated exchange with a saturated solution of copper sulphate, were even less active than sample II for the hydrogen-

deuterium exchange reaction.

X-ray diffraction traces taken on the samples after reaction showed some differences. The traces produced by sample I and the 80% exchanged zeolite showed that the catalysts had hardly any crystalline nature, only a small peak being evident at $2\theta = 6.5^\circ$. Sample II gave many peaks indicating that the catalyst after reaction was still crystalline. The major peak occurred at $2\theta = 32^\circ$ with other large peaks at 27° , 24° , 18° , 16° , and 14° . The peak at 6.5° however was only slightly bigger than that found in sample I. The trace for the 69% exchanged sample was similar to that for sample II. The Arrhenius parameters given in Table 3.3. are those for sample II since this was the most accurately prepared sample and had the greatest degree of crystallinity.

A similar unexpected difference in activity was found between two different samples of NiX. One sample (65% exch.) was active for hydrogen-deuterium exchange at room temperature giving a rate of $9.8\%/min/0.1g^*$ at $52^\circ C$ whereas another sample (68% exch.) gave a faster rate at $-94.6^\circ C$ ($12.3\%/min/0.1g$).

These samples were prepared from different batches of NaX and using different samples of nickel nitrate solution. However they were both prepared in exactly the same manner, and were both highly crystalline. The Arrhenius parameters

*This sample has also been used for studying the reactions of alkylbenzenes with deuterium. (45)

in Table 3.3. were those for the less active catalyst. The catalyst used for the exchange reactions of hydrocarbons however, was the more active version.

3.3. Results with Propylene/D₂O mixtures

Exchange

The exchange of propylene with heavy water was investigated on a number of ion exchanged sieves using small ratios of heavy water to propylene and low concentrations of reactants above the catalyst. Rates were measured by application of the equation[‡]:

$$\log_{10} (\phi_{\infty} - \phi) = \frac{-k_{\phi} t}{2.303 \phi_{\infty}} + \log_{10} (\phi_{\infty} - \phi_0)$$

The results are presented in Table 3.8. The amount of reactants added to the catalyst are expressed in molecules/a cage of the zeolite. In all cases this was kept as low as possible to minimise possible diffusion effects.

It was found that for NaX and the divalent cation exchanged forms (except CuX) a reaction mixture containing about 1 molecule D₂O and 0.5 molecules propylene per a cage of the zeolite gave a large enough partial pressure of propylene above the catalyst at reaction temperature to enable accurate analysis of the exchange reaction to be made using the mass spectrometric technique described earlier. However, for the trivalent cation exchanged forms of zeolite (CeX, LaX) the

[‡] see page 24.

Table 3.8. Arrhenius Parameters for the exchange of Propylene with D_2O on various cationic forms of X type zeolite.

Catalyst	% exch.	D_2O per cage	C_3H_6 per cage	Temp range of run ($^{\circ}C$)	E act (Kcal/mole)	$\log_{10} A$ (mole/sec 0.1g)	Temp $^{\circ}C$ for $k =$ 1.0%/min 0.1g
NaX	-	1.0 ± 0.1	0.6 ± 0.2	252 - 290	26.2 ± 2.0	26.9 ± 1.0	315
CaX	59	1.0 ± 0.1	0.7 ± 0.2	156 - 188	22.7 ± 2.0	28.0 ± 1.0	200
CoX	52	1.0 ± 0.1	0.5 ± 0.2	103 - 130	22.9 ± 2.0	30.0 ± 1.0	122
NiX	68	1.0 ± 0.1	0.5 ± 0.2	110 - 158	20.0 ± 2.0	28.3 ± 1.0	133
CuX	62	5.0 ± 0.1	2.0 ± 0.2	158 - 195	24.0 ± 2.0	30.0 ± 1.0	160
CeX	86	5.0 ± 0.1	2.5 ± 0.2	21 - 42	12.5 ± 2.0	26.3 ± 1.0	39
LaX	88	5.0 ± 0.1	2.5 ± 0.2	20 - 43	12.5 ± 2.0	26.6 ± 1.0	30
ThX	10	5.0 ± 0.1	2.5 ± 0.2	118 - 142	8.3 ± 2.0	21.4 ± 1.0	203

catalytic activity was such that larger amounts of reactants had to be used to counteract the increased adsorption at the lower temperatures used for exchange. The amounts given in Table 3.8. were just sufficient to enable accurate analysis of the exchange reaction to be carried out.

X-ray diffraction traces were taken of all the catalysts after reaction to test for crystallinity. In all cases the catalysts remained crystalline showing large peaks at $2\theta \approx 6^{\circ}$ whose intensity did not differ appreciably from those obtained from catalysts which had not undergone this treatment. The ThX zeolite was only exchanged to a small extent since

greater degrees of replacement of Na^+ for H^{++} led to structural collapse of the zeolite. Figure 3.10 shows the type of Arrhenius plots obtained with some of the zeolites.

Polymerisation

With some of these zeolites reactions other than pure exchange were taking place. This was inferred from the fact that the total amounts of isotopic propylenes in the gas phase were decreasing with time while the temperature of the reaction vessel and the sensitivity of the mass spectrometer remained constant. Figure 3.11 shows the variation of total propylene peak height with time for reaction at 110°C on NiX (68% exch.) in contact with D_2O and propylene concentrations equivalent to 1.0 and 0.5 molecules per α -cage respectively. Over the first 30 minutes reaction the total amount of gas phase propylene seemed to increase probably due to equilibration processes in the mass spectrometer. Afterwards the propylene started to disappear decreasing by 50% after 95 minutes. As shown in Figure 3.10 this disappearance of propylene followed first order kinetics giving a good straight line plot of \log_{10} (% propylene) versus time, 100% propylene being equated to the peak height after 60 minutes when all equilibration processes were assumed to be complete.

This disappearance of propylene did not affect the rate of exchange of propylene with D_2O as is demonstrated by the straight line nature of the ϕ plot in Figure 3.10. and so the

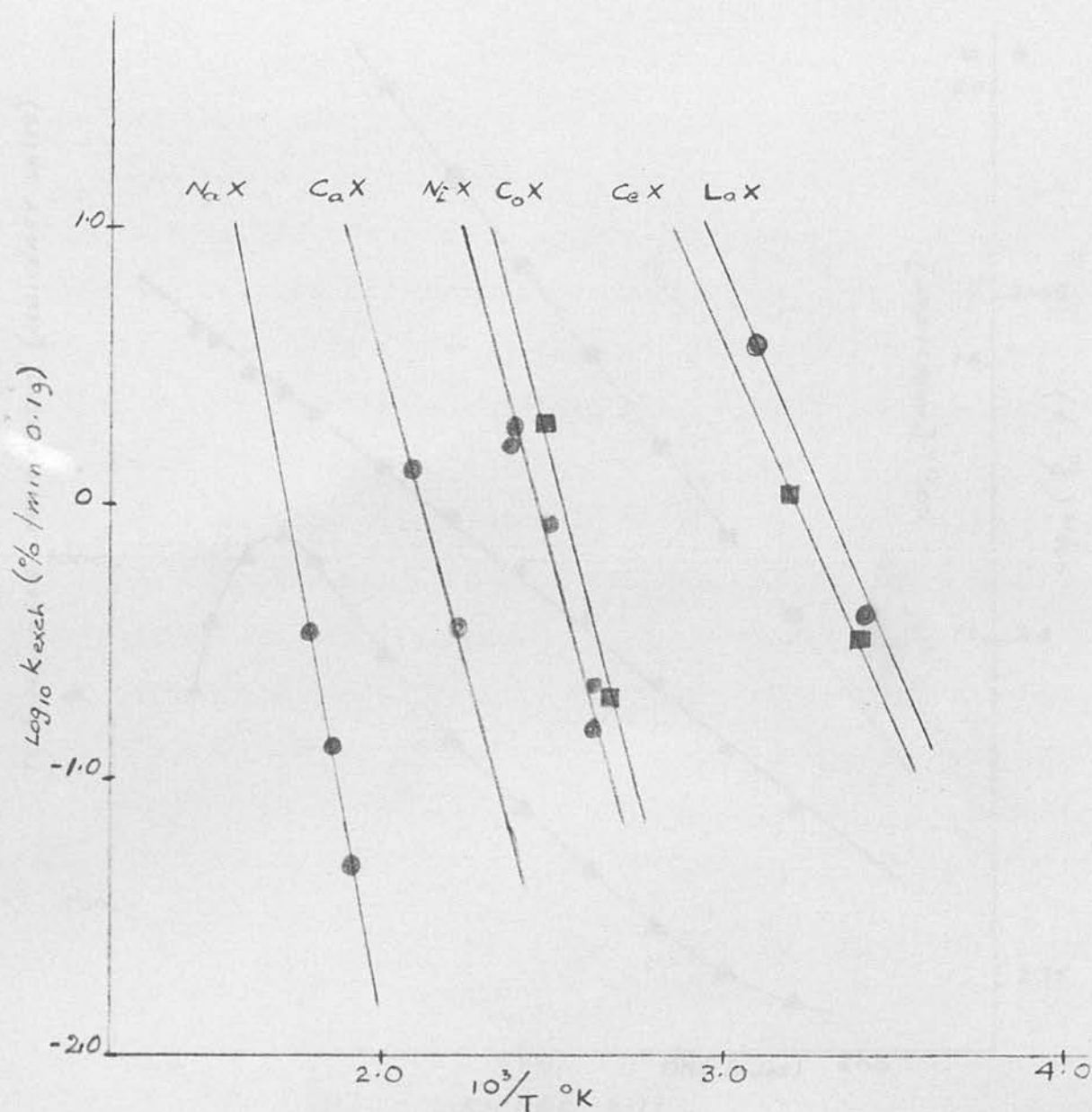


FIGURE 3.10

ARRHENIUS PLOTS FOR THE EXCHANGE OF PROPYLENE WITH D_2O ON X-TYPE ZEOLITES.

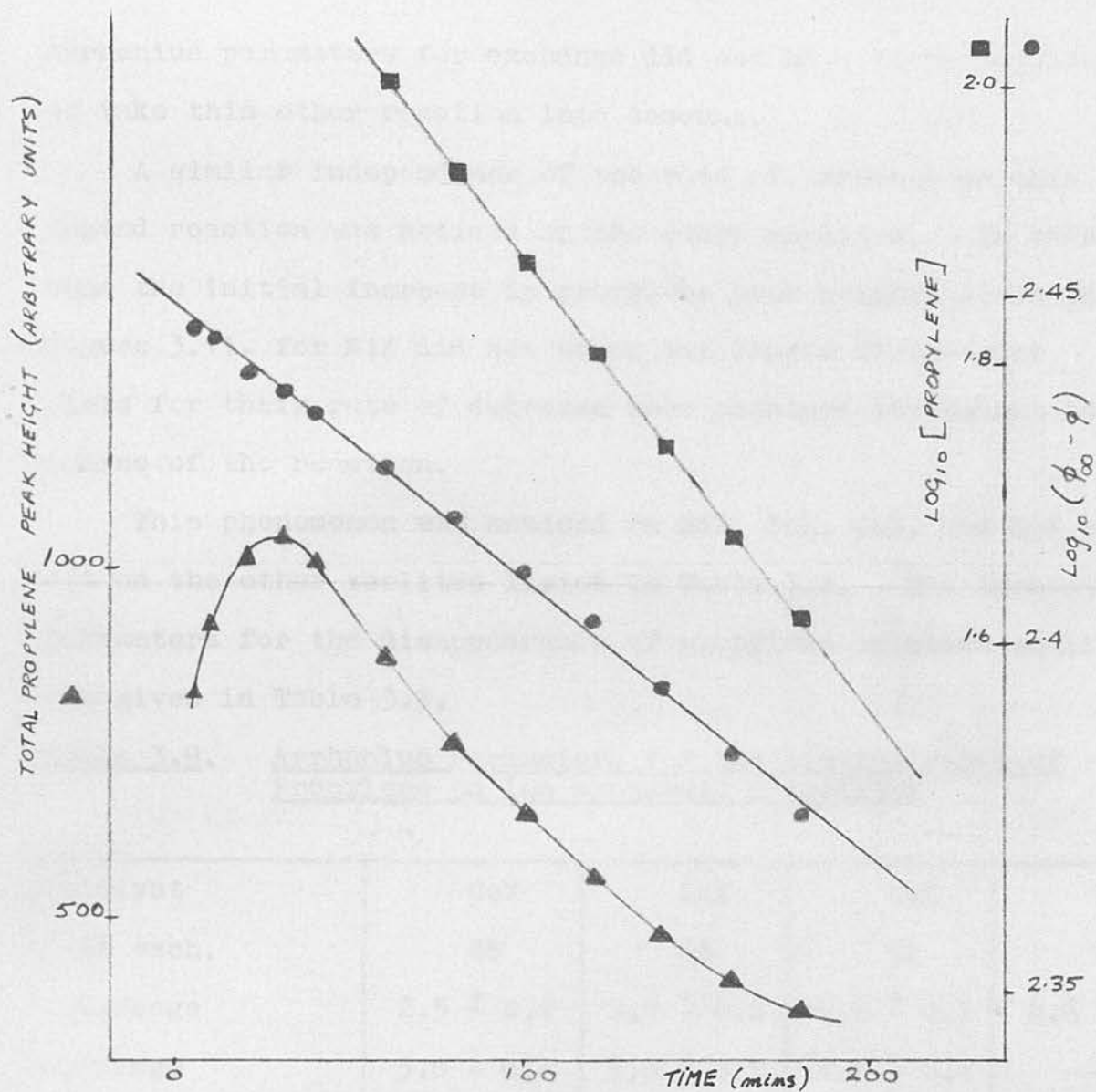


FIGURE 3.11

THE EXCHANGE & POLYMERISATION OF PROPYLENE ON NaX ZEOLITE

- ▲ TOTAL PROPYLENE PEAK HEIGHT
- FIRST ORDER RATE PLOT FOR EXCHANGE PROCESS
- " " " " " POLYMERISATION

Arrhenius parameters for exchange did not have to be adjusted to take this other reaction into account.

A similar independence of the rate of exchange on this second reaction was noticed on the other zeolites. In these runs the initial increase in propylene peak heights shown in Figure 3.11. for NiX did not occur and linear first-order plots for their rate of decrease were obtained throughout the course of the reaction.

This phenomenon was noticed on NiX, CuX, CeX, and LaX but not on the other zeolites listed in Table 3.8. The Arrhenius parameters for the disappearance of propylene on these zeolites are given in Table 3.9.

Table 3.9. Arrhenius Parameters for the disappearance of Propylene on ion exchanged X zeolites

Catalyst	CeX	LaX	CuX	NiX
% Na exch.	86	88	62	68
C ₃ H ₆ /cage	2.5 ± 0.2	2.5 ± 0.2	0.5 ± 0.2	0.6 ± 0.2
D ₂ O/cage	5.0 ± 0.1	5.0 ± 0.1	1.0 ± 0.1	0.0
Temp. range of reaction (°C)	21 - 42	20 - 48	24 - 88	99 - 136
E act (Kcal/mole)	12.5 ± 2.0	12.5 ± 2.0	12.0 ± 2.0	10.9 ± 2.0
Log ₁₀ A (mol/sec 0.1g)	26.3 ± 1.0	27.6 ± 1.0	25.3 ± 1.0	23.4 ± 1.0
Temp °C for k = 1.0%/min 0.1g	39	30	56	120

This disappearance of propylene was taken as evidence of a

polymerisation process. No reaction products could be detected at the temperatures where the rates of propylene disappearance were measured presumably because of their low volatility. However on further heating the catalysts, peaks at masses 57 - 60, 72 - 76 and ~ 84 were obtained from the mass spectrometer output and were attributed to the desorption of C_4 , C_5 and C_6 hydrocarbons from the zeolite surface.

The polymerisation reaction on CeX and LaX containing 5.0 molecules D_2O per cage had the same Arrhenius parameters as for exchange, both reactions occurring with similar rates at the same temperatures. With NiX the rate of polymerisation and exchange (1.0 molecules D_2O per cage) were similar at $110^\circ C$ but on raising the temperature the rate of polymerisation slowed down and curved rate plots were obtained. This was taken as evidence for a poisoning process, which on some runs also affected the rate of exchange. The Arrhenius parameters for NiX in Table 3.9. were obtained for an unpoisoned reaction where no D_2O was added to the catalyst. With CuX containing 1.0 molecules D_2O per cage the rate of polymerisation exceeded the rate of exchange so that the rate of exchange could not be measured with this concentration of D_2O . With the same sample of CuX with 2.5 molecules of propylene per cage and no added

D₂O a slower reaction occurred. This reaction had an activation energy of 7.7 Kcal/mole and a frequency factor of $\log_{10} A = 22.1$ molecules/sec 0.1g. In the presence of 5.0 molecules D₂O per cage there was no polymerisation.

Arrhenius plots for polymerisation are shown in Figure 3.12.

Effect of amount of D₂O added on the Arrhenius Parameters for exchange and Polymerisation

The effect of increasing the amount of D₂O on the catalyst activity for exchange of propylene was examined on NiX, CoX and CeX sieves. The results are presented in Table 3.11.

Table 3.11. Effect of D₂O content on the exchange of Propylene with heavy water on ion exchanged zeolites.

Catalyst	D ₂ O per cage	C ₃ H ₆ per cage	Temp range of rn. (°C)	E act (Kcal/mole)	Log ₁₀ A (mol/sec 0.1g)	Temp °C for k = 1.0%/min 0.1g
NiX (68% exch.)	1.0±0.1	0.5±0.2	110 - 158	20.0 ± 2.0	28.3 ± 1.0	133
	5.0±0.1	0.5±0.2	139 - 178	24.0 ± 2.0	29.4 ± 1.0	160
	11.1±0.1	0.5±0.2	135 - 168	41.1 ± 2.0	38.1 ± 1.0	165
CoX (52% exch.)	1.0±0.1	0.5±0.2	103 - 130	22.9 ± 2.0	30.0 ± 1.0	122
	9.5±0.1	1.2±0.2	132 - 161	35.7 ± 2.0	36.4 ± 1.0	143
	11.1±0.1	0.5±0.2	132 - 186	41.0 ± 2.0	38.1 ± 1.0	163
CeX (86% exch.)	5.0±0.1	2.5±0.2	21 - 42	12.5 ± 2.0	26.3 ± 1.0	39
	11.1±0.1	0.5±0.2	61 - 127	25.4 ± 2.0	32.3 ± 1.0	100

Increasing the amount of water poisons the exchange reaction at lower temperatures and raises the activation energy. The poisoning effect seems to be most severe at the lower D₂O

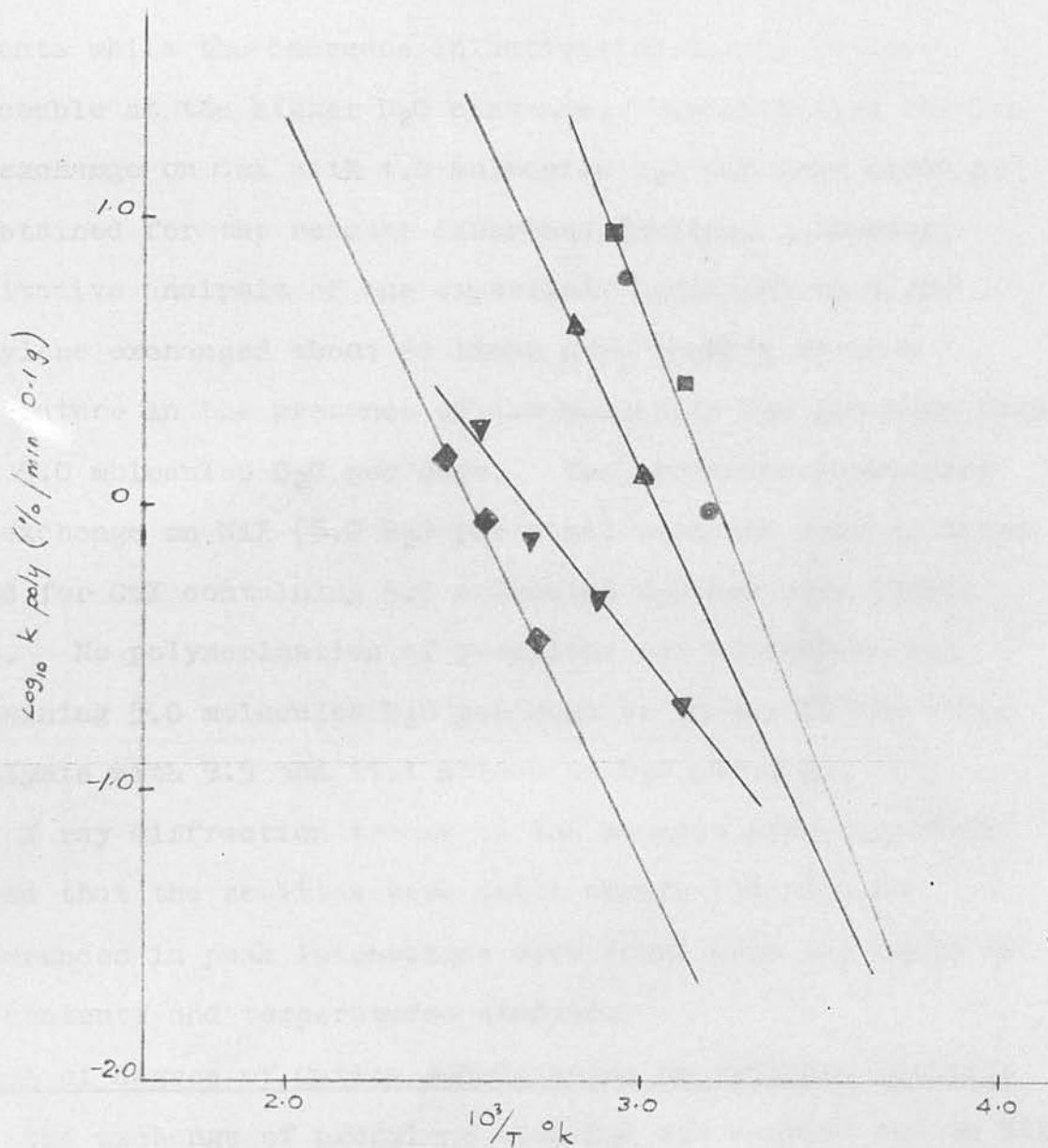


FIGURE 3.12

ARRHENIUS PLOTS FOR THE POLYMERISATION OF PROPYLENE ON ZEOLITES.

●	REACTION	ON	Ce X	CONTAINING	5.0	D ₂ O/cage.
■	"	"	La X	"	5.0	"
▲	"	"	Cu X	"	1.0	"
▼	"	"	Cu X	"	0.0	"
◆	"	"	Ni X	"	0.0	"

contents while the increase in activation energy is more noticeable at the higher D_2O contents. Quantitative results for exchange on CeX with 1.0 molecules D_2O per cage could not be obtained for the reasons described earlier. However, qualitative analysis of one experiment indicated that the propylene exchanged about 80 times more rapidly at room temperature in the presence of 1.0 molecules D_2O per cage than with 5.0 molecules D_2O per cage. The Arrhenius parameters for exchange on NiX (5.0 D_2O per cage) were the same as those found for CuX containing 5.0 molecules D_2O per cage (Table 3.8). No polymerisation of propylene was noticed on NiX containing 5.0 molecules D_2O per cage or on any of the other catalysts with 9.5 and 11.1 molecules D_2O per cage.

X ray diffraction traces on the samples after reaction showed that the zeolites were still crystalline and no differences in peak intensities were found over the range of D_2O contents and temperatures studied.

Effect of degree of Cation substitution on exchange activity

The exchange of propylene with D_2O was carried out on NiX and CeX zeolites containing different amounts of cations .

in order to determine the effect of increasing cation concentrations on the catalytic activity of the zeolite. The results in Table 3.12. show that the activity increases with the amount of cation present in the sieve. The trends in activation energies seem to be different for the two zeolites.

With CeX a pronounced decrease in activation energy is evident as one goes from the 24% exchanged zeolite to the 86% exchanged form. With NiX activation energy changes are small. In the temperature regions studied little evidence for polymerisation was found on any but the most highly ion exchanged forms of the two sieves.

Table 3.12. The exchange of propylene with D₂O on zeolites of different cation concentrations

Catalyst	% Na exchanged	D ₂ O per cage	C ₃ H ₆ per cage	Temp range of rn. (°C)	E act (Kcal/mole)	Log ₁₀ A (mol/sec 0.1g)	Temp for k = 1.0%/min 0.1g.
NaX	0	1.0±0.1	0.6±0.2	252 - 290	26.2±2.0	26.9±1.0	315
NiX	21	1.0±0.1	0.5±0.2	150 - 168	16.2±2.0	24.9±1.0	192
NiX	41	1.0±0.1	0.5±0.2	139 - 160	16.0±2.0	25.0±1.0	182
NiX	68	1.0±0.1	0.5±0.2	110 - 158	20.0±2.0	28.3±1.0	133
CeX	24	5.0±0.1	2.5±0.2	110 - 156	20.7±2.0	28.3±1.0	145
CeX	86	5.0±0.1	2.5±0.2	21 - 42	12.5±2.0	26.3±1.0	39

Nature of the exchange reaction

In all the exchange reactions of propylene on the various zeolites stepwise replacement of hydrogen by deuterium was evident, the only initial product being the monodeuterated species. In the experiments where large ratios of D₂O to hydrocarbon were used, the equilibrium amounts of the various isotopic species were large enough for calculations on the rate of exchange of the various hydrogen atoms in the molecule

to be carried out. This was done on the most highly exchanged forms of the NiX, CoX and CeX sieves. In each case only five of the six hydrogen atoms in propylene were readily exchangeable. Evidence for this was obtained from an inspection of isotopic distributions at various stages of the reaction. Table 3.13. shows a typical distribution after reaction on CoX, the propylene having almost reached its equilibrium deuterium content.

Table 3.13. Distribution of isotopic propylenes after reaction on CoX at 186°C for 2 hours.

Type	Percentage of isotopic species							ϕ
	d ₀	d ₁	d ₂	d ₃	d ₄	d ₅	d ₆	
Experimental	0.0	0.8	7.3	24.4	40.0	27.5	0.0	386.1
Calculated (5)	0.0	1.0	7.0	24.0	40.4	27.5	-	386.1
Calculated (6)	0.2	2.2	10.1	24.1	32.7	23.6	7.1	386.1

Large amounts of the d₅ isotope were present but the d₆ isotope was absent. Table 3.13. also shows distributions calculated on the assumption that five and six hydrogen atoms were exchanging by a stepwise process (calculated (5) and calculated (6) respectively). The close agreement between the experimental distribution and that calculated for 5 exchangeable hydrogens demonstrates the validity of the assumptions used in this calculation, viz. only five reactive positions in the propylene molecule, these five positions being in a state of equilibrium with each other.

The method used for calculating these isotopic distributions and the significance of the agreement between calculated and experimental distributions have been discussed in detail in Part II of this thesis.

The five exchangeable hydrogens in propylene were all found to react at the same rate. Evidence for this is shown in Figure 3.13. The experimental distributions obtained after discrete extents of reaction during the exchange reaction on the most highly exchanged forms of CoX, NiX and CeX, represented by the appropriate symbols, fall close to the lines which were calculated theoretically for the stepwise exchange of a molecule containing five equally reactive hydrogen atoms. Good agreement between theoretical and experimental distributions were found over the whole extent of reaction. If there had been differences in the individual rate of exchange of any of the five exchangeable hydrogen atoms in the propylene molecule this agreement would not have resulted.

The lines showing the theoretical variation of isotope concentrations with extent of reaction for a molecule containing five equally reactive hydrogens which are replaced in a stepwise manner were calculated from the appropriate terms of the binomial expansion of the expression:

$$100 \left(\frac{500 - \phi}{500} + \frac{\phi}{500} \right)^5$$

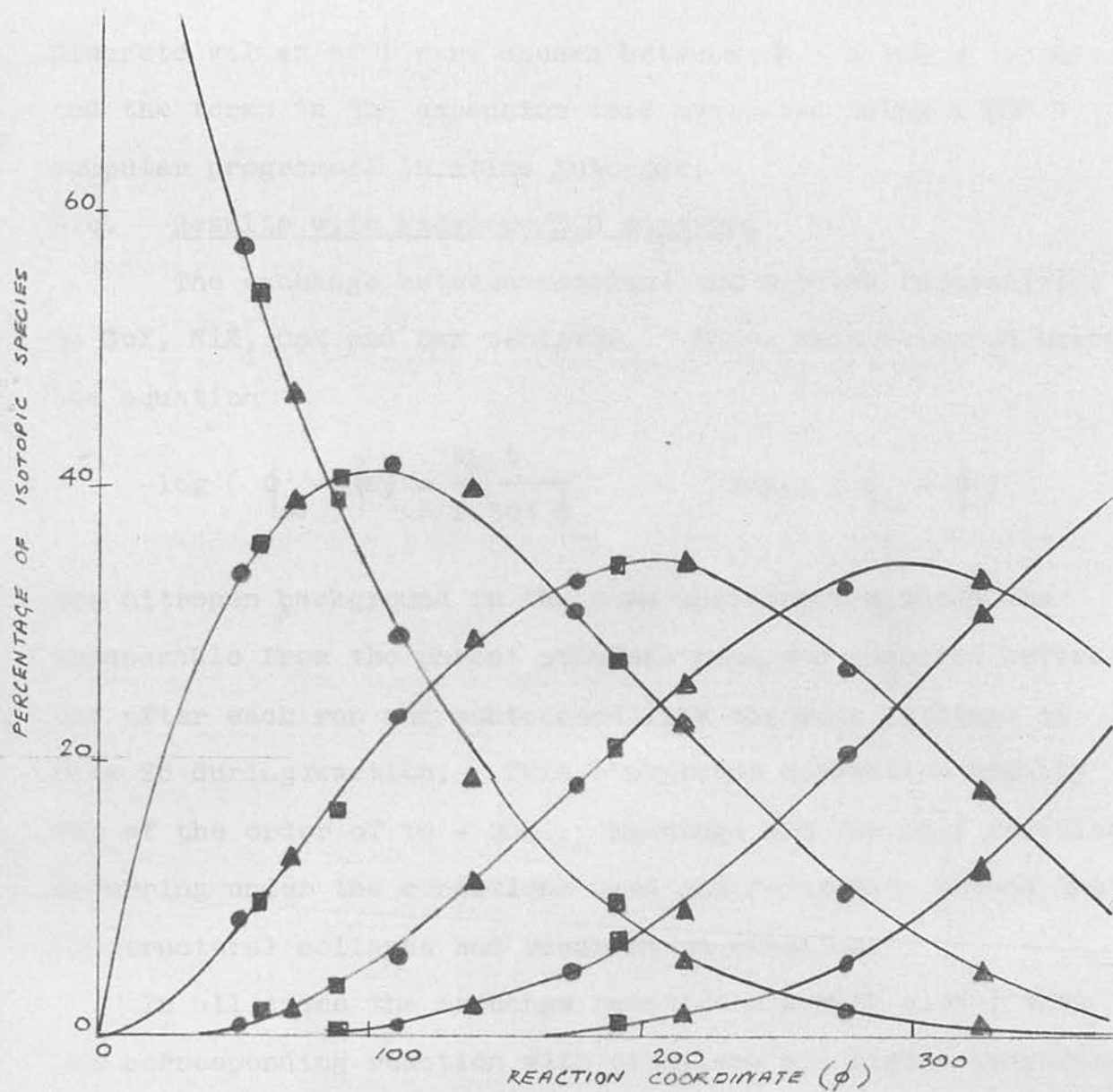


FIGURE 3.13

COMPARISON OF THEORETICAL DISTRIBUTIONS (LINES) FOR THE STEPWISE EXCHANGE OF FIVE EQUIVALENT HYDROGEN ATOMS AND EXPERIMENTAL DISTRIBUTIONS (POINTS) FOR THE EXCHANGE OF PROPYLENE WITH D_2O ON CoX (●), NiX (■) AND CeX (▲) ZEOLITES.

Discrete values of ϕ were chosen between $\phi = 0$ and $\phi = 360$ and the terms in the expansion were evaluated using a KDF 9 computer programmed in Atlas Autocode.

3.4. Results with Ethylene/D₂O mixtures

The exchange between ethylene and D₂O was investigated on CoX, NiX, CeX and LaX zeolites. Rates were measured using the equation

$$-\log \left(\phi_{\infty} - \phi \right) = \frac{k_{\phi} t}{2.303 \phi_{\infty}} - \log_{10} \left(\phi_{\infty} - \phi_0 \right)$$

The nitrogen background in the mass spectrometer, which was inseparable from the parent ethylene peak, was measured before and after each run and subtracted from the peak obtained at mass 28 during reaction. This background correction usually was of the order of 10 - 20%. Exchange was the only reaction occurring under the conditions used and X-ray data showed that no structural collapse had occurred on reaction.

In all cases the exchange reaction was much slower than the corresponding reaction with propylene and higher temperatures had to be used to obtain measureable rates of exchange. The results are summarised in Table 3.14.

The activities of CeX and LaX for the exchange of ethylene were very similar, both requiring a temperature of about 265°C to obtain the same reaction rate as was obtained with propylene exchange around 35°C. A similar decrease in activity was found for CoX. NiX however was more active than

Table 3.14. Arrhenius Parameters for the exchange of ethylene with D₂O on X type zeolites.

Catalyst	% exch.	D ₂ O per cage	C ₂ H ₄ per cage	Temp range of rxn. (°C)	E _{act} (Kcal/mole)	log ₁₀ A (mol/sec 0.1g)	Temp °C for k = 0.5%/min 0.1g
NiX	68	1.0±0.1	0.5±0.2	147 - 167	21.4±2.0	28.0±1.0	165
CoX	52	1.0±0.1	0.5±0.2	0.1 % / min	0.1 g. at 384°C		
CeX	86	5.5±0.1	2.5±0.2	214 - 252	22.0±2.0	26.5±1.0	265
LaX	88	5.0±0.1	2.5±0.2	204 - 290	23.9±2.0	27.3±1.0	267

CoX, the rate of exchange with ethylene being only about 10 times slower than that with propylene at 125°C and having a similar activation energy. For CeX and LaX the activation energies for exchange of ethylene (~23 Kcal/mole) were much higher than for propylene exchange (12.5 Kcal/mole).

Nature of the exchange reaction.

Table 3.15. shows some typical distributions of isotopic ethylenes at low extents of reaction on these zeolites. A comparison of these distributions with calculated distributions for a molecule containing four equally reactive hydrogens which are replaced in a stepwise manner, shows the experimental distributions to be slightly richer in the isotopes of higher deuterium content. Distributions at greater extents of reaction for CeX and LaX show that all four hydrogen atoms are exchangeable.

Table 3.15. Comparison of experimental and calculated product distributions for exchange of ethylene on zeolites.

Type	extent of Rn. ϕ	Percentage of isotopic species				
		d ₀	d ₁	d ₂	d ₃	d ₄
expt. on CeX	28.1	75.9	20.4	3.4	0.3	0.0
expt. on LaX	30.5	73.8	22.1	3.9	0.2	0.0
expt. on NiX	31.2	74.9	20.6	4.0	0.5	0.0
calculated	29.9	73.2	23.8	2.9	0.1	0.0
expt. on CeX	92.7	38.6	35.8	20.4	4.7	0.5
expt. on LaX	89.7	42.1	32.6	19.4	5.3	0.6
calculated	91.0	35.6	42.0	18.5	3.6	0.3

The difference between the experimental distributions and those calculated for stepwise exchange of a molecule containing four equivalent hydrogens could be due, in part, to inaccuracies introduced by assuming a statistical pattern for the fragmentation of the isotopic ethylenes (see page 48) or to the presence of a small amount of multiple exchange. However the discrepancies are small and considering the accuracy of analysis, may be wholly attributed to experimental error.

3.5. Results with 1-Butene/D₂O mixtures.

The exchange between 1-butene and D₂O was investigated on the most highly exchanged forms of CoX and CeX zeolites. The Arrhenius parameters for exchange in Table 3.16. show that the

exchange of 1-butene occurs in the same temperature range as propylene but the reaction has a lower activation energy.

Table 3.16. Rates and Arrhenius Parameters for the exchange of 1-butene with D_2O on zeolites.

Catalyst	% exch.	D_2O per cage	C_4H_8 per cage	Temp range of rn. ($^{\circ}C$)	E_{act} (Kcal/mole)	$\log_{10} A$ (mol/sec 0.1g)	Temp for $k = 1.0\%/min$ 0.1%
CoX	52	1.0 ± 0.1	0.5 ± 0.2	115 - 150	10.9 ± 2.0	23.6 ± 1.0	110
CeX	86	5.0 ± 0.1	2.5 ± 0.2	23 - 55	8.0 ± 2.0	23.8 ± 1.0	12

Nature of the exchange reaction

On both catalysts non random distributions of products were obtained during the initial stages of the reaction. Table 3.17 shows some typical distributions obtained after comparable stages of reaction on both catalysts. The large amount of d_1 in the initial products was taken to be indicative of a fast reaction leading to the preferential replacement of one hydrogen by deuterium in the molecule. Further evidence for this is shown by the fact that distributions, calculated assuming that one hydrogen reacts faster than the rest, agree well with the experimental distributions. These calculated distributions were obtained by the method described previously in Part II Chapter 3 of this thesis. Table 3.17. also shows distributions obtained from runs using 11.1 molecules D_2O and 0.5 molecules 1-butene per cage as reactants. These

Table 3.17. Comparison of experimental and calculated product distributions for the exchange of 1-butene on zeolites

Type	ϕ	Percentage of isotopic species								
		d ₀	d ₁	d ₂	d ₃	d ₄	d ₅	d ₆	d ₇	d ₈
expt. on CeX	70.4	40.0	50.7	8.3	0.9	0.1	0	0	0	0
Calc. (a)	51.6+18.4	40.1	50.5	8.7	0.7	0	0	0	0	0
expt. on CoX	70.1	44.0	43.4	11.1	1.5	0	0	0	0	0
Calc. (b)	42 + 28	43.6	44.2	10.8	1.4	0	0	0	0	0
Calc. (c)	70.1	48.0	36.9	12.4	2.4	0.3	0	0	0	0
expt. on CoX	413.7	0.3	2.4	9.6	20.8	27.6	22.4	11.8	4.3	0.8
expt. on CeX	406.1	0.0	2.2	13.0	23.9	25.5	18.4	9.5	4.8	2.7
calc. (c)	409.1	0.3	2.7	9.9	20.7	27.3	22.9	12.1	3.6	0.5

(a) (b). Calculated assuming 0.516 (a), and 0.42 (b), D atoms in one position with 0.184 (a), and 0.28 (b) D atoms distributed in a random fashion among the other seven positions.

(c). Calculated assuming all hydrogens equally reactive.

distributions show that all eight hydrogen atoms are exchangeable although in these runs also one hydrogen was preferentially replaced. The reaction on CoX containing 11.1 molecules D₂O per cage proceeded at a rate of 58.2%/min 0.1g at 187°C. Curved rate plots were obtained on reaction over CeX which were attributed to a poisoning process.

Reaction occurred at 57°C giving an initial rate of 1.32%/min/0.1g.

Polymerisation

Polymerisation occurred on CeX, but not on CoX, when the lower coverages of D₂O were used. With CeX the polymerisation reaction occurred at a rate of 1%/min 0.1g at 19°C. The activation energy of the reaction was 13.2 Kcal/mole and the frequency factor was calculated to be $\log_{10} A = 27.5$ molecules/sec 0.1g. The polymerisation process, like that for propylene on CeX, did not affect the exchange process. Little polymerisation was found in the run using 11.1 molecules D₂O/cage.

On all runs at higher temperatures the 1-butene decomposed to give products whose spectra occurred in the butene mass range. This could account for the greater than statistical amounts of the higher deuterioisotopes in Table 3.19. since corrections to account for the superimposition of the two spectra could not be made. No other products could be detected at 52°C on CeX containing 1.0 molecules D₂O/cage. With CeX containing 11.1 molecules D₂O/cage other products at masses 85 - 90 and ~ 100 were observed at 155°C.

3.6. Results with Isobutene/D₂O mixtures

The exchange between isobutene and D₂O was investigated on 0.1 g samples of CoX and CeX zeolites. On reaction on CoX (52% exch.) containing 1.0 molecules D₂O per cage and the

equivalent of 0.75 molecules isobutene per cage reaction took place very readily at 20°C, equilibrium being attained in about two minutes. A similar activity was found on reaction on CeX (86% exch.) containing 11.1 molecules D₂O/cage. Results obtained from reactions carried out using larger amounts of D₂O adsorbed on the catalysts, where the poisoning effect of the D₂O and the decreased adsorption of the hydrocarbon enabled rates and Arrhenius parameters to be measured, and summarised in Table 3.18.

Table 3.18. Rates and Arrhenius Parameters for the exchange of isobutene with D₂O on zeolites.

Catalyst	% Na exch	D ₂ O per cage	C ₄ H ₈ per cage	Temp range of Rn. (°C)	E act (Kcal/mole)	log ₁₀ A (mol/sec 0.1g)	Temp (°C) for k = 1.0%/min 0.1g
CoX	52	11.1±0.1	0.5±0.2	0 - 44	15.3±2.0	29.3±1.0	7
CeX	86	19.5-0.1	3.0-0.1	1.9% / min	0.1 g. at 21.4°C		

The reaction on CeX seemed to be poisoned and so Arrhenius parameters could not be determined. On CoX at higher temperatures (~ 50°C) reactions other than exchange were occurring leading to a decrease in the amount of isobutene in the reaction vessel.

Nature of exchange reaction.

Exchange occurred in a stepwise manner on both catalysts leading to the replacement of all eight hydrogen atoms in the

hydrocarbon. Table 3.19. shows some typical distributions of products obtained during reaction.

Table 3.19. Comparison of experimental and calculated product distributions for the exchange of isobutene on zeolites

Type	ϕ	Percentage of isotopic species								
		d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
expt. on CoX	65.0	50.2	35.9	12.2	1.7	0.0	-	-	-	-
Calculated ^(a)	69.0	48.6	36.7	12.1	2.3	0.3	0.0	-	-	-
Expt. on CeX	68.9	51.7	32.5	11.8	3.1	0.9	0.0	-	-	-
expt. on CoX	413.2	0.3	4.9	9.1	18.6	26.0	22.6	13.1	5.0	0.5
Calculated ^(a)	409.1	0.3	2.7	9.9	20.7	27.3	22.9	12.1	3.6	0.5
expt. on CeX	335.1	2.2	9.8	19.7	24.5	21.4	13.0	6.3	2.8	0.3
Calculated ^(a)	330.1	1.4	8.0	19.6	27.5	24.1	13.6	4.7	1.0	0.1

(a) Calculated assuming stepwise exchange and eight equally reactive hydrogen atoms.

Although the experimental distributions are subject to some error due to the difficulty of analysis the close resemblance between experimental and calculated distributions demonstrate that all eight hydrogen atoms in the molecule react at similar rates.

3.7. Results with isobutane/D₂O mixtures.

The exchange between isobutane and D₂O was investigated on CoX, NiX, CeX and LaX zeolites. CoX and NiX were inactive

for exchange, giving only a small reaction on prolonged heating at about 400°C, so the Arrhenius parameters for exchange could not be determined. CeX and LaX had similar activities and were much more active than the CoX and NiX zeolites. The reaction parameters for exchange using rates determined from the equation

$$-\log (\phi_{\infty} - \phi) = \frac{k_{\phi} t}{2.303 \phi_{\infty}} - \log (\phi_{\infty} - \phi_0)$$

are summarised in Table 3.20.

Table 3.20. Rates and Arrhenius parameters for exchange of isobutane with D₂O on zeolites

Catalyst	% exch	D ₂ O per cage	C ₄ H ₁₀ per cage	Temp range of rn. °C	E act (Kcal/mole)	Log ₁₀ A (mol/sec 0.1g)	Temp °C for k = 1.0%/min 0.1g.
CeX	86	5.0±0.1	2.5±0.2	226-358	9.2±1.0	21.3±0.5	262
LaX	88	5.0±0.1	2.5±0.2	217-273	9.2±1.0	21.2±0.5	267
CoX	52	1.0±0.1	0.5±0.2	~5% reaction after 2 hours at 420°C			
NiX	68	1.0±0.1	0.5±0.2	~6% reaction after 4 hours at 400°C			

The activities of CeX, LaX and CoX for exchange of isobutane are similar to those found for the exchange of ethylene on the same catalysts. Both reactions occur in the same temperature regions although the activation energy is lower in the case of isobutane exchange.

Nature of the exchange reaction

The reaction between isobutane and D_2O gave large amounts of polydeuterated species in the initial products. For CeX and LaX the M value of the exchange reaction was about 8 at $230^\circ C$ and increased with temperature. For NiX and CoX M values of 2 - 3 were found. Table 3.21. shows some distributions of isotopic isobutanes found during the initial stages of the reaction.

Table 3.21. Distribution of isotopic isobutanes from the reaction of isobutane with D_2O on zeolites.

Catalyst	ϕ	Percentage of isotopic species											M
		d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	
CeX	51.2	93.3	0.0	0.0	0.0	0.0	0.0	0.0	3.0	3.1	0.6	0.0	7.6
LaX	55.2	92.8	0.0	0.0	0.0	0.0	0.0	0.0	2.9	3.3	1.0	0.0	7.6
NiX	22.4	93.4	1.6	0.8	0.8	1.4	1.0	0.8	0.2	0.0	0.0	0.0	3.4
CoX	10.7	94.7	3.6	0.3	0.2	0.4	0.5	0.3	0.0	0.0	0.0	0.0	2.0

Although some difficulty was found in applying the correct fragmentation factors, analysis of the results showed that on CeX and LaX the major initial products were the d_7 , d_8 and d_9 isotopes, the amounts of the d_1 - d_6 isotopes being negligible with the d_{10} isotope absent. With NiX and CoX product maxima were found at the d_1 and d_4 - d_5 isotopes. The change in product distribution with increasing extent of reaction is

shown in Figure 3.14. for reaction on LaX. The large increase in the d_1 and d_6 isotopes at higher extents of reaction is due to the onset of equilibrium ($\phi_{eq} = 250$) and the partial establishment of interconversion equilibria between the various isotopic species.

3.8. Results with m-Xylene/D₂O mixtures

The exchange between m-xylene and D₂O was investigated on CoX (52% exch.) and CeX (86% exch.) zeolites. The reaction mixture added to 1/10 g samples of the catalysts in the reaction vessel was equivalent to 11.1 molecules D₂O and 2.0 molecules m-xylene per cage of the zeolite. The reaction was studied by adjusting the furnace controls so that a constant rate of heating ($\sim 1.2^\circ\text{C}/\text{min}$) was obtained. Figures 3.15 and 3.16 show the way in which the various isotopic species vary with time and temperature over the two catalysts.

In both cases there were differences in the relative rates of reaction of the various hydrogen atoms in the molecule. The hydrogens could be divided into three groups of 3, 1 and 6 atoms each in order of ~~increasing~~^{de} reactivity. Table 3.22. shows the large build up of products at the d_3 and d_4 isotopes at different stages of the reaction compared with those calculated assuming ten equally reactive hydrogen atoms (calculated^(b)). Comparison of distributions at early stages of the reaction show that the first three hydrogens to react, do so with equal rates and by a stepwise process since

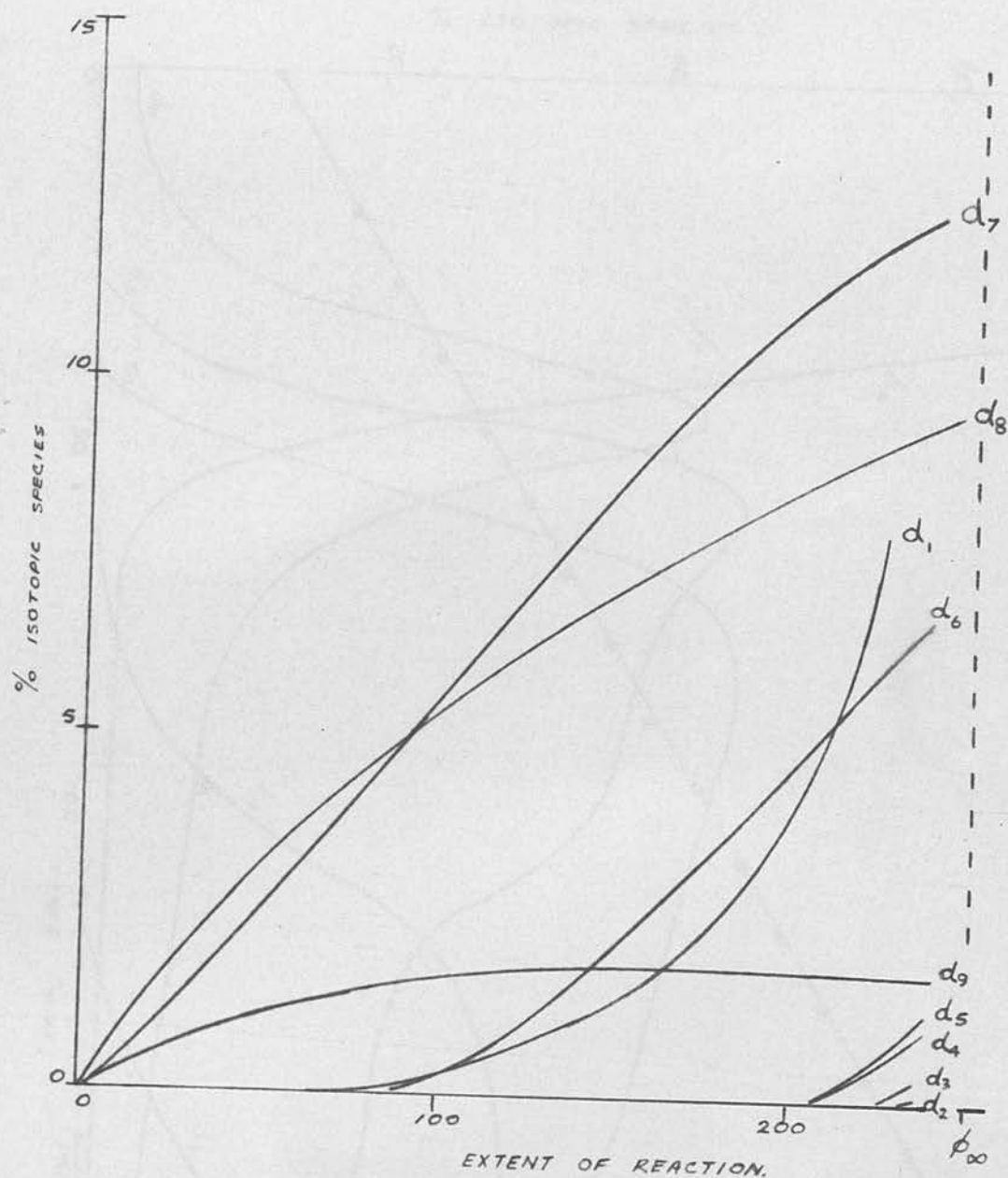


FIGURE 3.14

THE DISTRIBUTION OF ISOTOPIC SPECIES WITH EXTENT OF REACTION FOR EXCHANGE OF ISOBUTANE WITH D_2O ON LaX . $\phi_{\infty} = 250$.

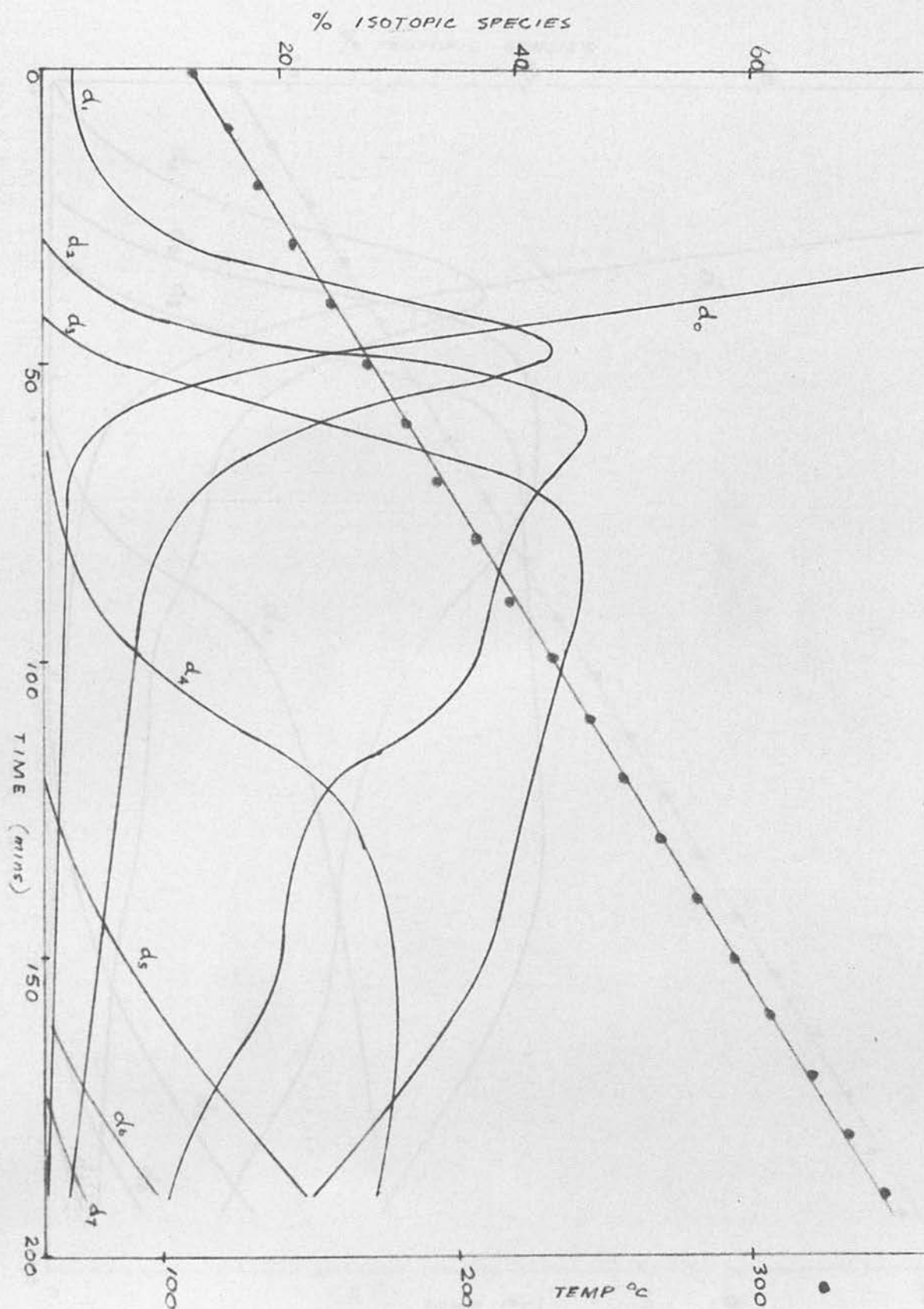


FIGURE 3.15

THE EXCHANGE OF m -XYLENE WITH D_2O ON C_0X ZEOLITE

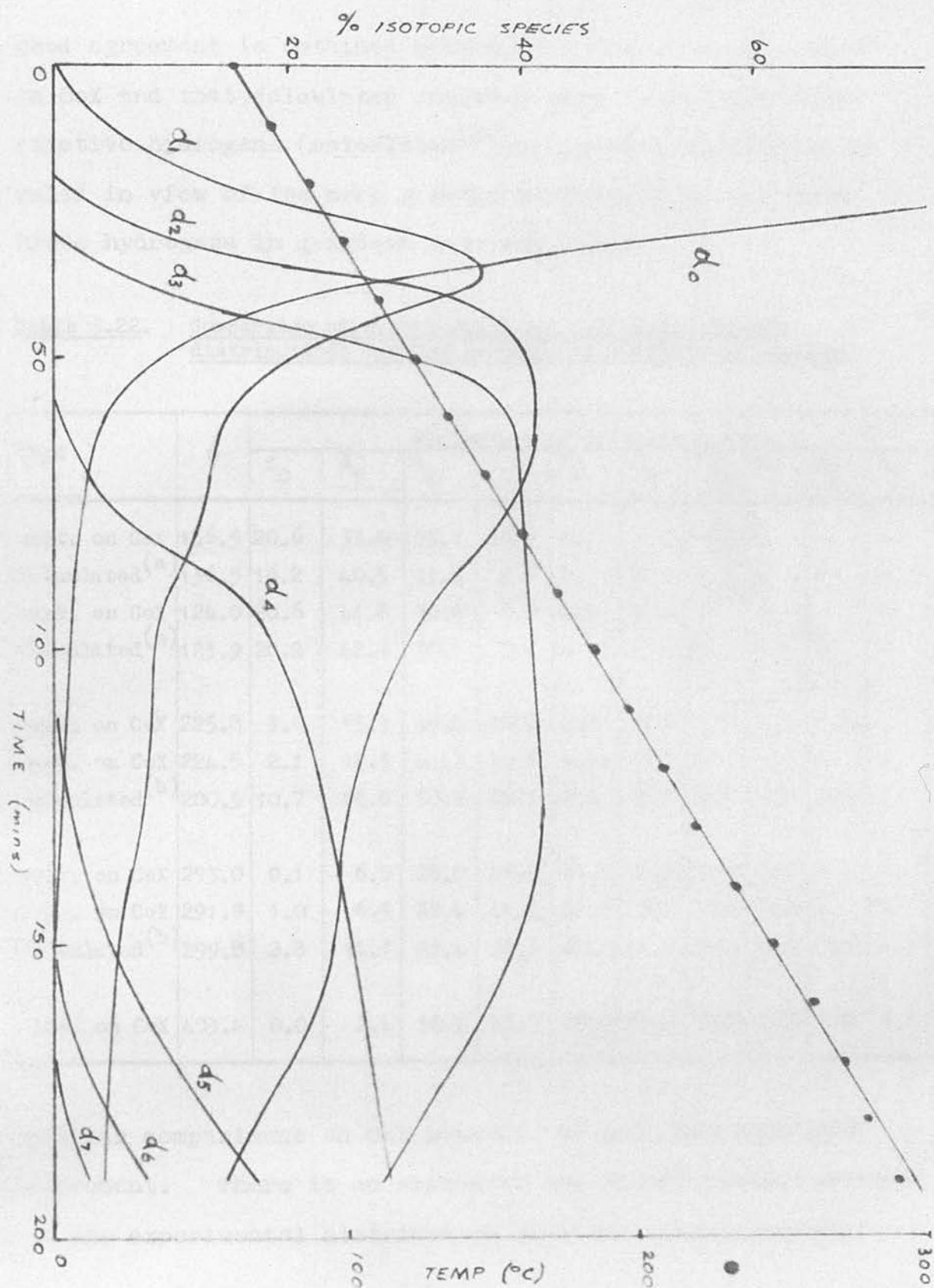


FIGURE 3.16

THE EXCHANGE OF *m*-XYLENE WITH D_2O ON C_2X ZEOLITE.

good agreement is obtained between the experimental result on CoX and that calculated assuming only three equivalent reactive hydrogens (calculated^(a)). Such a comparison is valid in view of the much greater reactivity of the first three hydrogens in *m*-xylene over any other.

Table 3.22. Comparison of experimental and calculated product distributions for the exchange of *m*-xylene on zeolites

Type	ϕ	Percentage of isotopic species										
		d ₀	d ₁	d ₂	d ₃	d ₄	d ₅	d ₆	d ₇	d ₈	d ₉	d ₁₀
expt. on CeX	136.5	20.6	33.0	35.7	10.7	0.0	-	-	-	-	-	-
Calculated ^(a)	136.5	16.2	40.5	33.9	9.4	-	-	-	-	-	-	-
expt. on CoX	124.0	20.6	41.8	30.6	7.0	0.0	-	-	-	-	-	-
Calculated ^(a)	123.9	20.2	42.7	30.1	7.0	-	-	-	-	-	-	-
expt. on CeX	225.8	3.0	13.7	40.8	39.5	3.0	0.0	-	-	-	-	-
expt. on CoX	224.5	2.1	14.5	41.7	40.2	1.5	0.0	-	-	-	-	-
Calculated ^(b)	200.5	10.7	26.8	30.2	20.1	8.8	2.7	0.6	0.1	0.0	-	-
expt. on CeX	293.0	0.1	6.0	25.0	41.6	24.5	2.6	0.2	0.0	-	-	-
expt. on CoX	291.9	1.0	6.9	22.4	41.4	25.6	2.6	0.1	0.0	-	-	-
Calculated ^(b)	299.8	2.8	12.1	23.4	26.7	20.0	10.3	3.7	0.9	0.1	-	-
expt. on CoX	403.4	0.0	2.4	10.9	23.2	28.0	21.0	9.9	3.7	0.8	0.1	0.0

Similar comparisons on CeX however, do not give such good agreement. There is an excess of the higher deuterioisotopes in the experimental distribution over the calculated one.

This may be due to the presence of a certain amount of multiple exchange but is more likely to be associated with diffusion processes in the zeolite pores, which, if they limit the rate of the reaction, would be expected to give distributions similar to those found.

On both catalysts the last six hydrogens to react exchanged with similar rates. This is shown by the relative amounts of the d_5 to d_{10} isomers illustrated above for CoX at $\phi = 403.4$ ($\phi_\infty = 550$). ϕ Plots are shown for both catalysts in Figure 3.17.

3.8. Results with hydrocarbon/deuterium mixtures.

The reactions of propylene and ethylene with deuterium gas were investigated on NiX zeolite. This zeolite was chosen for study since the hydrogen-deuterium exchange reaction was rapid on this catalyst (12.3%/min 0.1g at -94.5°C) and thus the results obtained were more likely to be indicative of the hydrocarbon adsorption processes rather than the ability of the catalyst to supply suitably activated deuterium to the system.

With propylene/ D_2 and ethylene/ D_2 mixtures on NiX deuteration of the olefin occurred along with exchange. This introduced complications in analysis by the mass spectrometric technique used and the results, presented in Table 3.23. are of a semi-quantitative nature only. The reaction with propylene was carried out on 0.1 gms. NiX using

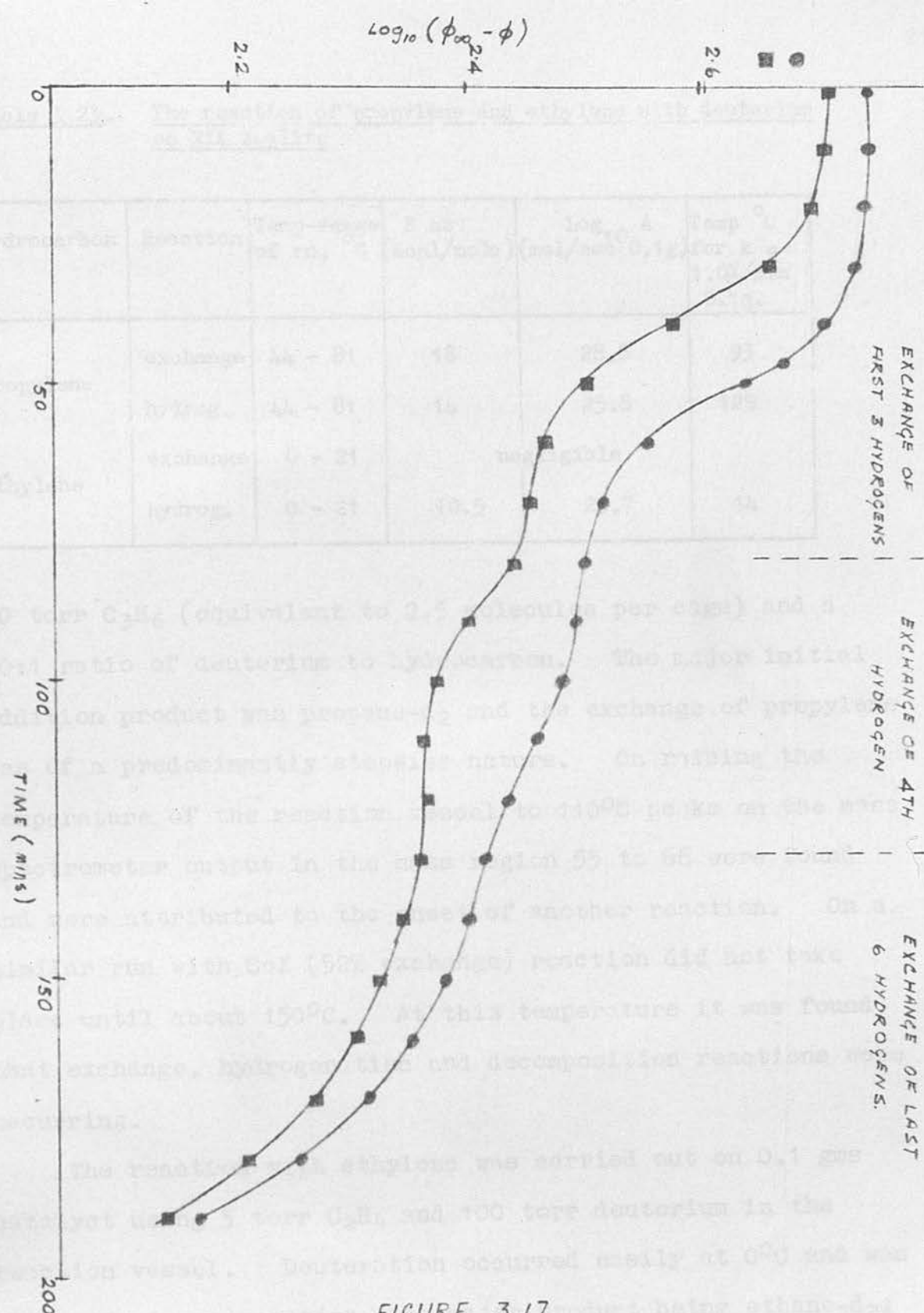


FIGURE 3.17

ϕ PLOTS FOR THE RISING TEMPERATURE EXCHANGE OF m-XYLENE WITH D_2O ON CoX (●) AND CeX (■) ZEOLITES.

Table 3.23. The reaction of propylene and ethylene with deuterium on NiX zeolite

Hydrocarbon	Reaction	Temp range of rn. °C	E act (Kcal/mole)	Log ₁₀ A (mol/sec 0.1g)	Temp °C for k = 1.0%/min 0.1g.
propylene	exchange	44 - 81	18	28.8	93
	hydrog.	44 - 81	14	25.8	125
ethylene	exchange	0 - 21	negligible		
	hydrog.	0 - 21	10.5	25.7	14

10 torr C_3H_6 (equivalent to 2.5 molecules per cage) and a 10:1 ratio of deuterium to hydrocarbon. The major initial addition product was propane- d_2 and the exchange of propylene was of a predominantly stepwise nature. On raising the temperature of the reaction vessel to 110°C peaks on the mass spectrometer output in the mass region 55 to 66 were found and were attributed to the onset of another reaction. On a similar run with CoX (52% exchange) reaction did not take place until about 150°C. At this temperature it was found that exchange, hydrogenation and decomposition reactions were occurring.

The reaction with ethylene was carried out on 0.1 gms catalyst using 5 torr C_2H_4 and 100 torr deuterium in the reaction vessel. Deuteration occurred easily at 0°C and was the predominant reaction, the major product being ethane- d_2 ; exchange was negligible compared with the deuteration reaction.

On raising the temperature to 170°C the ethane- d_2 started to decompose giving products at approximate masses 47, 63 and 84. Exchange of ethane did not take place until around 190°C . At this temperature multiple exchange occurred giving ethane d_6 as the major product.

A preliminary run with isobutene and deuterium on NiX showed that deuteration of this molecule also occurred at 0°C .

CHAPTER 4

Discussion

4.1. Hydrogen - Deuterium exchange

The reaction between H_2 and D_2 to form HD according to the equation:

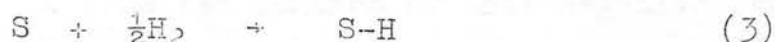
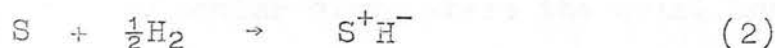
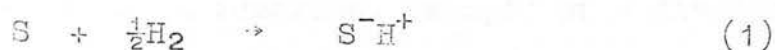


has been investigated on many catalysts, particularly metals and metal oxides.^(198,199) It was found that the reaction was first order and that the activation energy was very low. This is in contrast to most of the results reported here for the reaction on ion exchanged zeolites where relatively high activation energies were found.

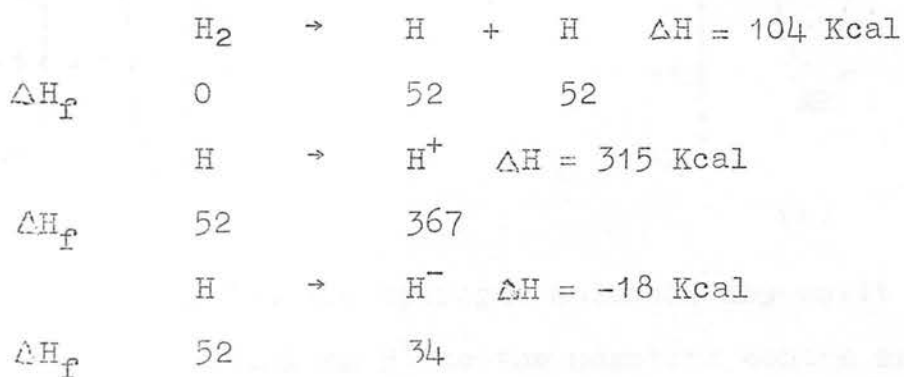
There is a wide difference in the views of various authors on the mechanism of this reaction. Three hypotheses have been proposed. The first is the Bonhoeffer-Farkas mechanism⁽²⁰⁰⁾ according to which both hydrogen and deuterium molecules are chemisorbed and dissociated on the catalyst surface. The second is the Rideal mechanism,^(201,202) according to which the reaction proceeds between a chemisorbed atom and a physically adsorbed molecule. The third is the Schwab mechanism,^(203,204) according to which the reaction takes place between two adsorbed and strongly polarised molecules. The different mechanisms are possibly applicable under different reaction conditions; the Bonhoeffer-Farkas mechanism may apply at higher temperatures

while the Rideal mechanism may apply at lower temperatures.

By analogy with the bonding in free molecules, the chemisorbed bond may be either predominantly ionic or covalent. Thus for chemisorption of hydrogen on a catalyst surface (S), possible reactions are:



Energy is expended in the dissociation of the hydrogen molecule and in cases (1) and (2) converting these atoms into ions. The energy changes associated with these processes for one mole reactant are:

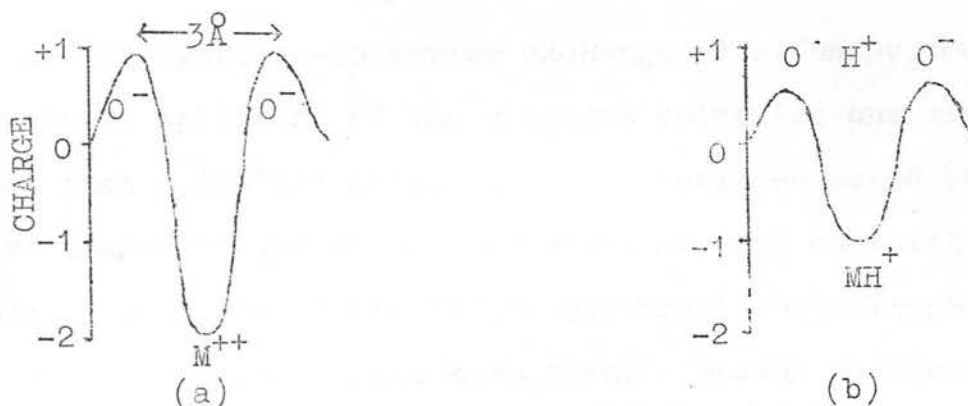


(ΔH_f = heat of formation at 25°C)

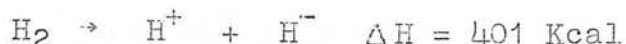
It has been shown⁽²⁰⁵⁾ that for the chemisorption of hydrogen on tungsten the energy expended is greater than the energy gained by 200 and 115 Kcal/g. atom for processes (1) and (2) respectively thus making them unfavourable in view of the high endothermicity of the reaction. For tungsten it has

been suggested that the bond is essentially covalent.

For metal exchanged zeolites however, the process may be different to that found on pure metals. The large field gradients caused by the localisation of electronic charges may tend to produce heterolytic splitting of molecules on adsorption. If we take an idealised example of a divalent metal exchanged X type molecular sieve where the metal ion is situated equidistant from two centres of unit negative charge about 3\AA apart⁽¹⁶⁹⁾ then the charge distributions at these sites is as depicted below (a).



On chemisorption the hydrogen molecule may split heterolytically adding an H^+ to the negative centre and an H^- to the positive centre (b). This process would result in a lowering of the energy of the zeolite surface and the energy gained may offset the higher energy required to split a hydrogen molecule heterolytically over that for the homolytic process.



The fact that most zeolites are poor catalysts for the hydrogen-deuterium exchange reaction could be attributed to the fact that the hydrogen molecule has no permanent dipole and the tendency of the zeolite to produce heterolytic splitting. The more active samples of NiX and CuX zeolites display results which are different from the general trend and seem to be more metal-like with regard to their relatively high activity and low activation energy.

If the hydrogen-deuterium exchange reaction proceeds via heterolytic splitting of the reactant molecules one might expect that trivalent metal exchanged zeolites would be more active than divalent ones. However, no such correlation exists. This may be due to the different relative positions of the ions in the zeolite structure. Recent evidence⁽²⁰⁶⁾ has suggested that in trivalent exchanged sieves the metal ions are paired which is different from the case with divalent exchanged forms. Also the gain in energy in converting M^{+++} to MH^{++} may not differ substantially from the process $\text{M}^{++} \rightarrow \text{MH}^+$.

In view of the fact that different preparations of CuX and NiX had such marked differences in activity it is doubtful whether any conclusions concerning reactivities should be drawn from the data in Table 3.3. Turkovich⁽²⁰⁷⁾ has suggested that

impurities such as TiO_2 , ZnO_2 or Fe_2O_3 may be responsible for the activity of partially decationised faujasites for the hydrogen-deuterium exchange reaction. However, a difference in such impurity levels cannot be invoked to explain the different activities of the CuX zeolites since they were all prepared from the same starting materials. The difference in activity of the two NiX samples cannot be explained in terms of differences in crystallinity as their X-ray diffraction traces were similar. Obviously there must be some subtle differences in the catalysts which have a profound effect on the hydrogen-deuterium exchange activity but more work will be required in order to elucidate further the nature of these differences.

The increase in catalytic activity on raising the outgassing temperature probably reflects the poisoning effects of adsorbed water which may be held on the active site for exchange and effectively lower the energy heterogeneity of the surface. The subsidiary reaction leading to the dilution of deuterium in the gas phase 'hydrogen' on CoX outgassed at 200°C is probably due to exchange with this adsorbed water. Thus the two reactions occurring may be:



The rates measured by the increase in the amount of HD in the gas phase corresponds to the sum of the absolute rates of both reactions. Thus the rates measured for the hydrogen-

deuterium exchange reaction in these experiments should be lowered by ~10% to account for the HD produced by the reaction with adsorbed water. Such a correction leads to even better agreement than that shown in Figure 3.6, for the rates of exchange of the two reactions, identical rates being obtained when both processes were measured at the same time. The fact that both the exchange of deuterium with hydrogen and with adsorbed water occur at the same rate and with the same activation energy suggests a common slow step which is probably connected with the activation of gas phase "hydrogen".

At the temperatures used for exchange ($100 - 185^{\circ}\text{C}$) the adsorbed water is likely to be immobile since it was not removed on evacuation at 200°C and so the hydrogen-deuterium exchange reaction must take place on the sites where the adsorbed water is located. Rabo⁽¹⁷⁰⁾, Habgood⁽²⁰⁸⁾ and Ward⁽¹⁹³⁾ have suggested that water is preferentially adsorbed on the zeolite cations. This is in keeping with the previous suggestion concerning the locus of the sites where hydrogen-deuterium exchange might take place. Surface OH groups may be intermediates common to both reactions.

From the extent of dilution of the deuterium it is possible to calculate the amount of water taking part in the reaction as follows:

Total amount of $\text{H}_2 + \text{D}_2$ in reaction vessel $\approx 1.56 \times 10^{20}$
molecules

Initial %H = 48.6 $\approx 7.6 \times 10^{19}$ molecules

Final %H = 58.4 $\approx 9.12 \times 10^{19}$ molecules

∴ amount of H coming from reaction with adsorbed water =
 3.04×10^{19} atoms

assume $\sim 45\%$ replacement of H by D in water

∴ amount of water present = 3.38×10^{19} molecules
 $= 1.01 \times 10^{-3}$ gms as H_2O

Catalyst wt = 0.107 gms hydrated (0.079 gms dehydrated)

no of α cages $\approx 2.7 \times 10^{19}$

∴ amount of exchangeable water on catalyst = 1.26%
 ≈ 1.25 molecules/
 α cage.

These results are in reasonable agreement with other values quoted in the literature for the amount of residual water in partially dehydrated zeolites. Topchieva et al.⁽¹⁸²⁾ report values corresponding to about 0.6% and 3.5% water remaining respectively on 22% and 85% decationated Y zeolites outgassed at 200°C and Barrer et al.⁽¹⁶⁶⁾ report a value of 0.6% water for NaX. Pope and Kemball⁽⁴⁸⁾ however, find a higher value (4.3%) for NiX which they attribute to a greater ion-dipole interaction.

Figure 4.1. shows how the activity of the CoX sieve varies with the degree of replacement of sodium ions by cobalt ions. The proportionally larger increase in activity after small degrees of exchange cannot readily be explained in terms of

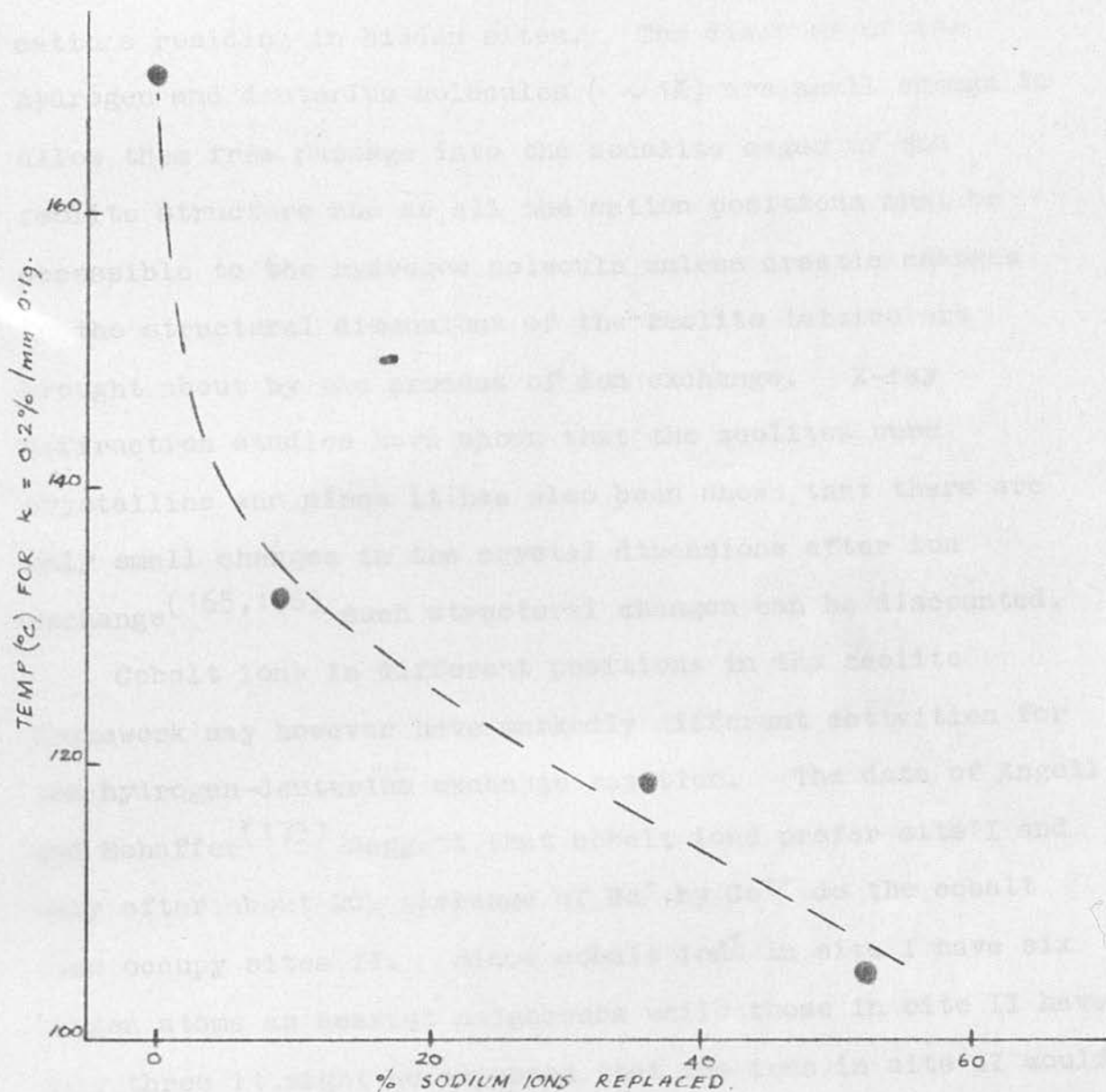


FIGURE 4.1

VARIATION IN CATALYTIC ACTIVITY FOR THE HYDROGEN/DEUTERIUM EXCHANGE REACTION WITH INCREASING DEGREE OF REPLACEMENT OF Na^+ BY Co^{++} IONS IN X-TYPE ZEOLITES.

cations residing in hidden sites. The diameter of the hydrogen and deuterium molecules ($\sim 1\text{\AA}$) are small enough to allow them free passage into the sodalite cages of the zeolite structure and so all the cation positions must be accessible to the hydrogen molecule unless drastic changes in the structural dimensions of the zeolite lattice are brought about by the process of ion exchange. X-ray diffraction studies have shown that the zeolites were crystalline and since it has also been shown that there are only small changes in the crystal dimensions after ion exchange^(165,166) such structural changes can be discounted.

Cobalt ions in different positions in the zeolite framework may however have markedly different activities for the hydrogen-deuterium exchange reaction. The data of Angell and Schaffer⁽¹⁷⁵⁾ suggest that cobalt ions prefer site I and only after about 20% exchange of Na^+ by Co^{++} do the cobalt ions occupy sites II. Since cobalt ions in site I have six oxygen atoms as nearest neighbours while those in site II have only three it might be expected that the ions in site II would hold water more strongly than those in site I in order to preserve their preferred co-ordination number. Adsorption of water would effectively lower the energy heterogeneity of this site and thus make it less active for heterolytic splitting of hydrogen atoms.

On the other hand subsidiary processes which may occur

along with ion exchange may be important in determining the catalytic activity of the zeolite although in this context it must be borne in mind that a similar procedure to that used for ion exchange was carried out on NaX in the form of a blank with deionised distilled water. However, the anomalous behaviour of the NiX and CuX preparations, mentioned previously, lends some support to the suggestion that in certain cases the activity of the zeolite may only depend to a minor extent on the exchanged ion.

The nature of the acceleratory reactions found on CoX, MnX and CaX zeolites are not well understood. These results seem to be opposed to those of Turkevich et al.⁽²⁰⁷⁾ where hydrogen treatment of synthetic faujasites at 250°C for 30 mins. destroyed the catalytic activity for hydrogen-deuterium exchange. It has been reported⁽²⁰⁹⁾ that on treatment with hydrogen the metal ions present in zeolites can be reduced to the elemental state and form atomic dispersions or small crystallites of metal. Pope and Kemball⁽⁴⁸⁾ noticed that hydrogen treatment of a NiX zeolite enhanced the catalytic activity for benzene hydrogenation. This change in nature of the catalyst which was reversible on evacuation after treatment at 300°C but irreversible after treatment at 350°C was attributed to reduction processes which ultimately produced nickel atoms from nickel ions. However, the experimental observations reported here are difficult to correlate with reduction processes.

Cu^{++} ions would be expected to be easier to reduce than Co^{++} Ca^{++} or Mn^{++} ions but hydrogen treatment of CuX at 300°C produced no change in catalytic activity while marked acceleratory effects were noticed on similar treatments of CoX at 150°C and CaX and MnX at 235°C . Higher temperatures would also be expected to be required to effect reduction of these latter ions.

Nevertheless there is a real change in the nature of the catalyst which cannot be reversed simply by evacuation. It may be that the process occurring involves some migration or displacement of ions or adsorbed water molecules. The fact that a CoX zeolite outgassed at 296°C shows a more pronounced acceleration at $\sim 150^{\circ}\text{C}$ than the same zeolite outgassed at 395°C or 497°C indicates that adsorbed water may play a part in the reaction. The ability of deuterium to exchange with this residual water shows that interaction can take place. Perhaps the adsorbed water, which is probably in the form of OH groups, may become mobile on interaction with a suitably chemisorbed hydrogen ion. Migration of the water to another part of the zeolite crystal may expose and strengthen the active site for exchange. The greater acceleration noticed on the CoX zeolite outgassed at 296°C may be attributed to (a) the greater ease of removal of this bound water and (b) the greater amount of water being removed.

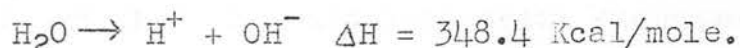
If this water is associated with the cation one might

expect a correlation to exist between the strength of the cation-water bond and the temperature required for the acceleration process. The standard hydration energies for Ca^{++} , Mn^{++} , Co^{++} and Cu^{++} ions are 140, 80, 30 and 20 Kcal/mole respectively.⁽²¹⁰⁾ Thus one would have expected this reaction to have taken place easily on CuX which was not found. However, CuX may be anomalous and also the cation may play another role in this reaction.

Another explanation for the acceleratory reaction could be because strongly chemisorbed oxygen not removed on evacuation deactivates the catalyst and this oxygen may be removed on treatment with hydrogen. Turkevich⁽²⁰⁷⁾ has shown that adsorbed oxygen poisons the hydrogen-deuterium exchange reaction on Y type sieves and Hall⁽²¹¹⁾ has shown that this oxygen can be removed by hydrogen treatment although in so doing the ability of the catalyst to form carbonium ions from phenylated amines is destroyed. More work is needed to elucidate further the mechanism of this acceleration. It might be informative to test whether the catalyst still retains its 'superactivity' after rehydration. Other techniques such as I.R. and E.S.R. may also prove useful in probing these effects.

4.2. Activity Pattern for the reactions of hydrocarbons with D_2O .

Since most of the zeolites used in this work were poor catalysts for the hydrogen-deuterium exchange reaction there is the possibility that the activity of the catalysts with regard to the exchange between hydrocarbons and deuterium gas would be controlled by the ability of the zeolite to supply suitably activated deuterium to the system. As it was hoped to examine the activity of the catalysts as a function of the hydrocarbon used a more active source of deuterium had to be sought. Dehydrated zeolites are known to have a high affinity for water⁽¹⁷⁸⁾ and so D_2O was chosen as a source of deuterium for reaction with hydrocarbons.



$$\Delta H_f \quad -57.8 \quad +367 \quad -76.4$$

The reaction schemes above show that the energy required to split the water molecule heterolytically is 53 Kcal/mole less than that required to heterolytically cleave the hydrogen molecule. Also the fact that the water molecule has a permanent dipole which can align with the electrostatic fields on the zeolite surface whereas hydrogen has no such dipole should make D_2O the better source of deuterium for exchange with hydrocarbons if adsorption proceeds via heterolytic splitting

of the molecules.

Infra-red data on the adsorption of water on zeolite surfaces has suggested that such a heterolytic process does occur.⁽¹⁹³⁾ The results obtained in this work show that D₂O is easier to activate than D₂ since the exchange between isobutene and D₂O occurs very readily at temperatures up to 200°C - 300°C lower than that required for hydrogen-deuterium exchange. In all the work reported here concerning the reactions of hydrocarbons the catalytic activity can be taken as being indicative of the adsorption processes of the hydrocarbon alone.

The activity of the zeolites for the exchange of hydrocarbons seem to fall into groups according to the charge on the cation, with the exception of CaX which has an activity intermediate between NaX and the other divalent metal exchanged forms. The activity increases and the apparent activation energy decreases with increasing charge on the cation present in the zeolite. Figure 4.2. shows how the activation energy for the exchange of propylene varies with cation parameters. The function $Z^2/r_{\text{eff.}}$ was taken to correlate the trend where Z is the cation charge and $r_{\text{eff.}}$ is the effective distance from the centre of the cation to the adsorbed reactant molecule. This term which appears in the theoretical calculation of single ion hydration energies based on the simple Born equation⁽²¹⁰⁾ has previously been used to make similar correlations for formic

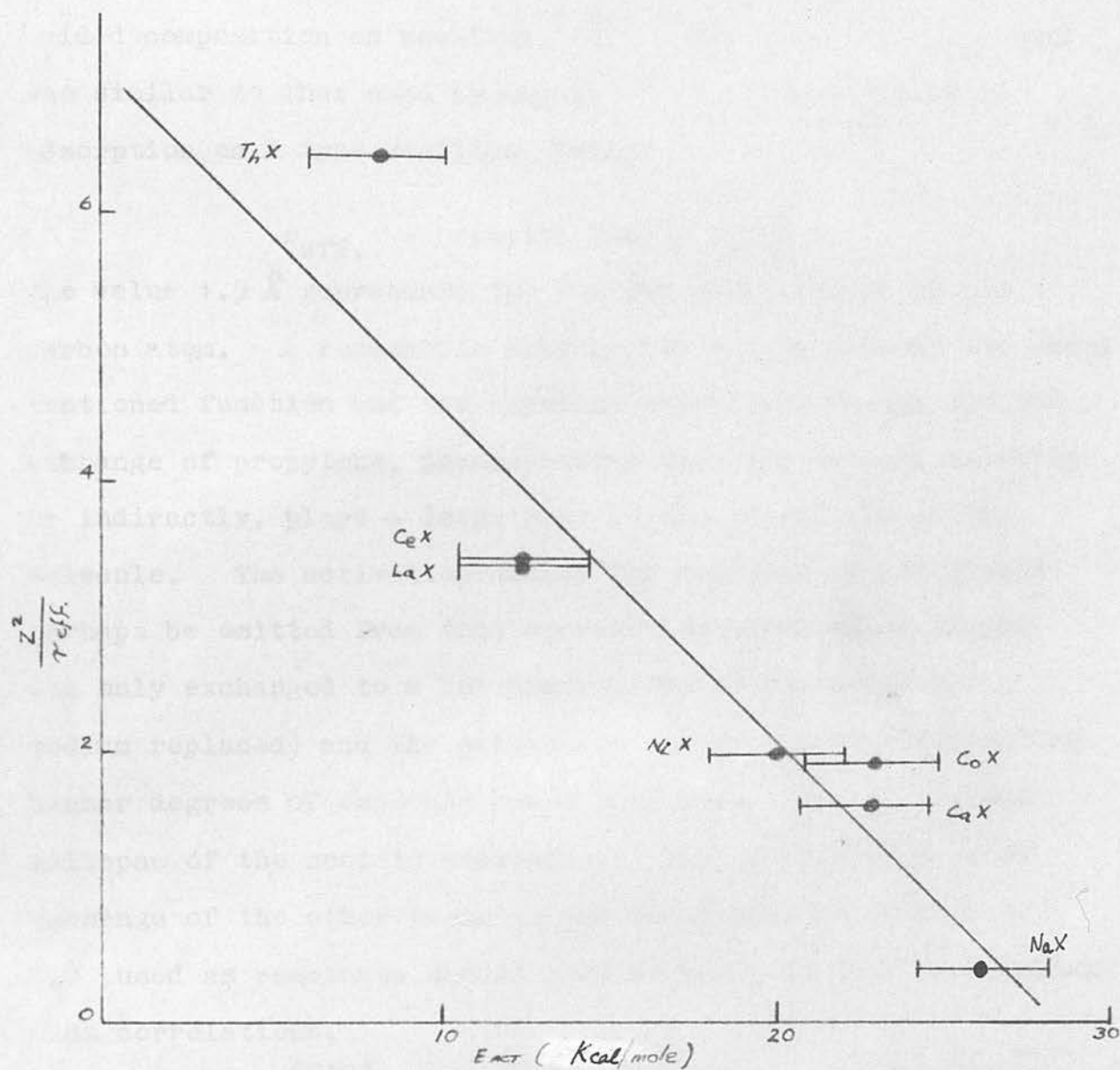


FIGURE 4.2

VARIATION OF THE ACTIVATION ENERGY FOR EXCHANGE OF PROPYLENE WITH D_2O WITH A FUNCTION OF THE CATIONIC CHARGE FOR X-TYPE ZEOLITES.

acid decomposition on zeolites.⁽¹⁹⁵⁾ The value of r_{eff} , used was similar to that used by Angell⁽¹⁷⁵⁾ in the study of CO adsorption on X type zeolites, being:

$$r_{\text{eff.}} = r(\text{metal ion}) + 1.5 \text{ \AA}$$

The value 1.5 \AA represents the Van der Waals radius of the carbon atom. A reasonable correlation exists between the above mentioned function and the apparent activation energy for the exchange of propylene, demonstrating that the cation, directly or indirectly, plays a large part in the activation of the molecule. The activation energy for reaction on ThX should perhaps be omitted from this correlation since the catalyst was only exchanged to a low degree (10% of the available sodium replaced) and the activation energy may be different if higher degrees of exchange could have been achieved without collapse of the zeolite structure. The varying degrees of exchange of the other zeolites and the different amounts of D_2O used as reactants should also be borne in mind when making such correlations.

Richardson⁽²¹²⁾ has shown that there is a correlation between the activity of zeolites for electron transfer processes and the electron affinity of the exchanged cation. The electron affinities of the Na^+ , Ca^{++} , Co^{++} , Ni^{++} , Ce^{++} and La^{+++} ions, deduced from their ionisation potentials,⁽²¹⁰⁾ are 5.1, 11.9, 17.0, 18.2, 19.7 and 19.2 eV respectively. There is a

rough correlation between these values and the activation energies for the exchange of propylene on the corresponding ion exchanged zeolites although as Richardson has pointed out the free ion ionisation potentials only reflect in a qualitative sort of way the electron affinities of the ions in a solid matrix. The reaction parameters for the exchange of propylene also parallel the trend in total acidities which have been measured for similar zeolites by Nishizawa et al.⁽¹⁸³⁾ who report values of 0, 0.04 and ~ 0.4 meq./g. for NaX, CaX and CeX (LaX) respectively.

The activities of the various zeolites for the exchange of propylene with D₂O are similar to those which have recently been reported for the isomerisation of 1-butene over X type zeolites.⁽¹⁸³⁾ In this case, as in the work reported here, the order of activity of the zeolites was CeX, LaX > CaX > NaX. These authors also studied the activity of the zeolites for the polymerisation of propylene and ethylene. In most cases the polymerisation of ethylene was much slower than that of propylene. Their results for propylene polymerisation also parallel those found in this work, NaX and CaX having no activity, NiX moderate activity and CeX and LaX high activity at 200°C. However their values for the activities of NiX, CeX and LaX were much lower than those found here.

Figure 4.3. shows how the activity of the CeX zeolite varies with the hydrocarbon used. The order of reactivity for

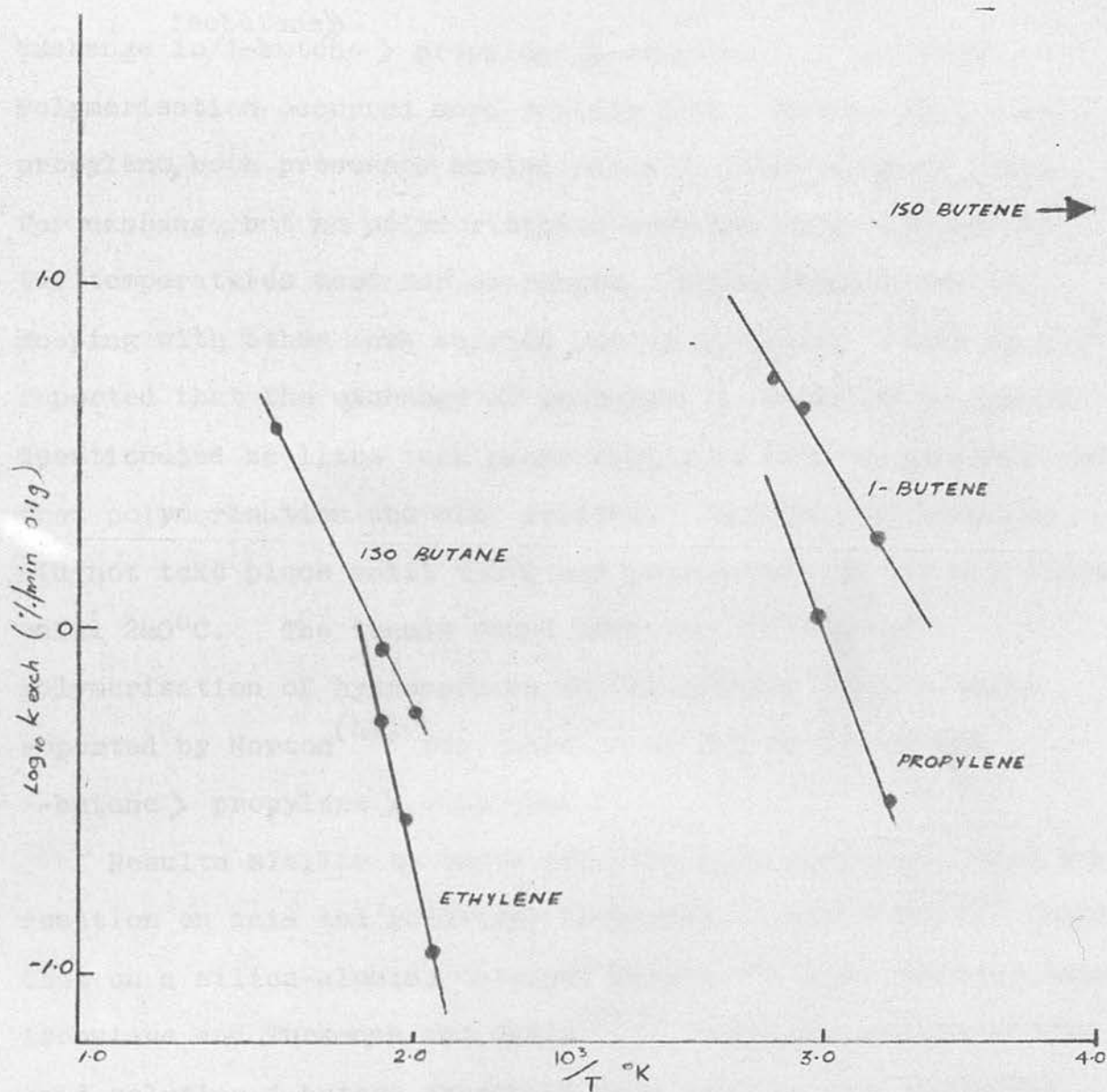


FIGURE 4.3.

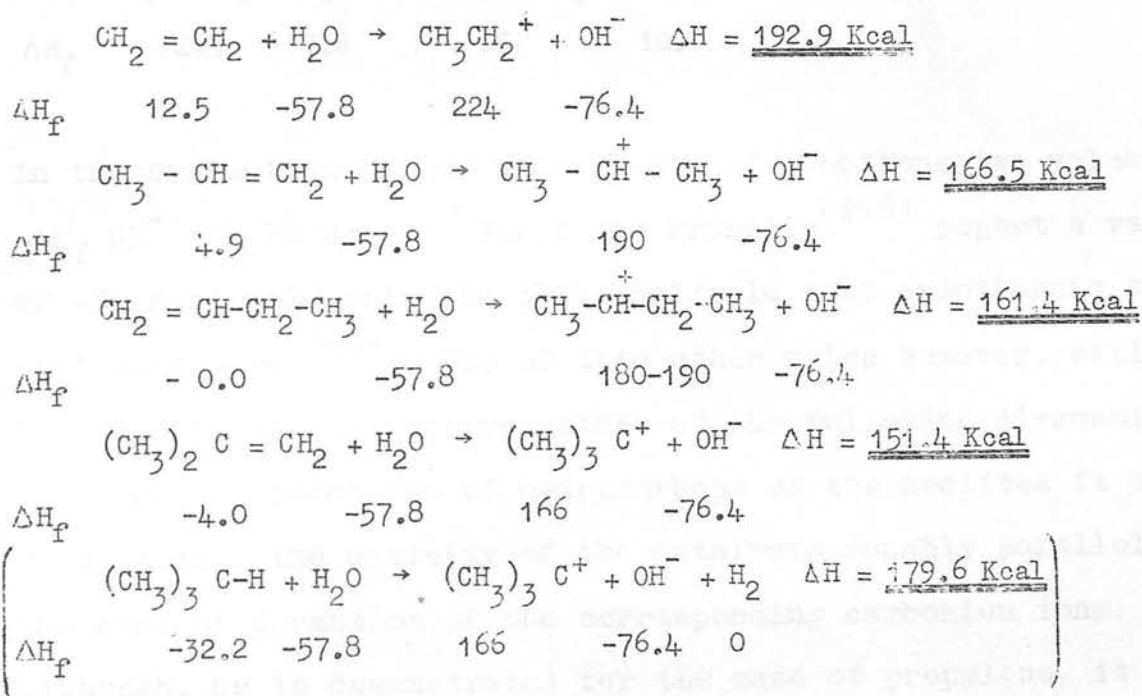
ARRHENIUS PLOTS FOR THE EXCHANGE OF HYDROCARBONS WITH D_2O ON C_{6X} ZEOLITE (2.5 MOLECULES HYDROCARBON AND 5.0 MOLECULES D_2O PER CAGE)

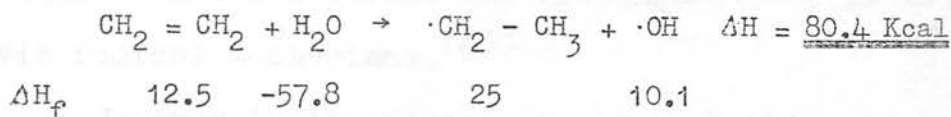
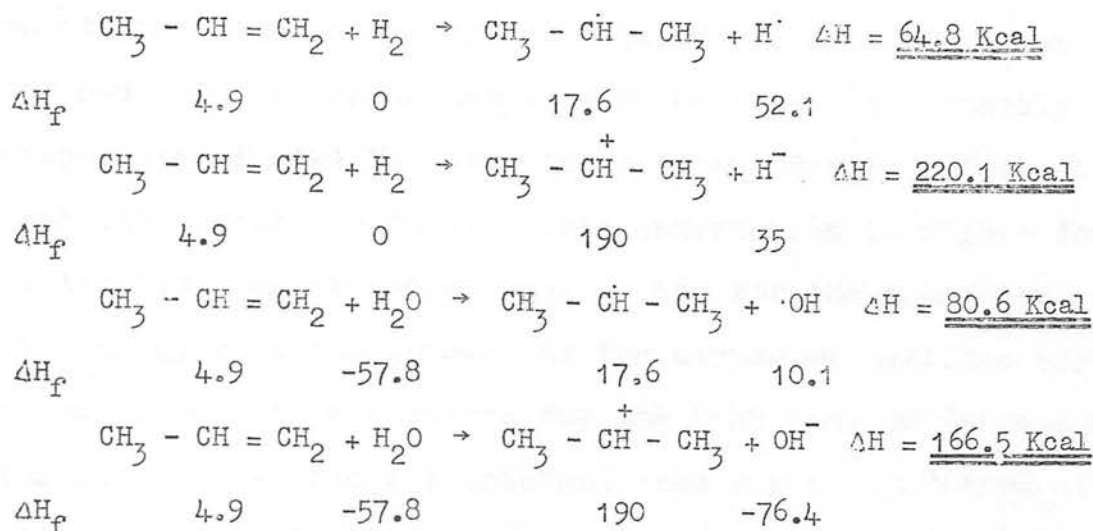
isobutene exchange is/isobutene > propylene >> ethylene and isobutane. Polymerisation occurred more rapidly with 1-butene than with propylene, both processes having rates similar to those found for exchange, but no polymerisation occurred with ethylene at the temperatures used for exchange. These results are in keeping with other work carried out on zeolites. Hall et al.⁽¹⁹⁰⁾ reported that the exchange of propylene with the OD groups of decationated zeolites took place easily at room temperature and that polymerisation was also evident. Exchange of ethylene did not take place until 150°C and polymerisation did not start until 240°C. The trends found here for the ease of polymerisation of hydrocarbons on CeX are the same as those reported by Norton⁽⁴¹⁾ for reaction on CaX zeolite being 1-butene > propylene > ethylene.

Results similar to those reported here have been found for reaction on acid and acid-type catalysts. Hansford⁽¹³⁰⁾ found that on a silica-alumina catalyst butene was more reactive than isobutane and Turkovich and Smith⁽²¹³⁾ found that in phosphoric acid solution 1-butene exchanged more rapidly than propylene and that no reaction occurred with ethylene. The activation energies for the exchange of 1-butene and propylene were 17.8 and 19.6 Kcal/mole respectively and exchange was accompanied by polymerisation.

In acid catalysis the hydrocarbons react via carbonium ion intermediates and it is likely that the same intermediates

occur on reaction on zeolites under the conditions used in this work. Thus if, as has often been suggested,⁽¹³⁰⁾ the formation of this carbonium ion intermediate is the rate determining step, the pattern of activity for the various hydrocarbons should reflect the ease of formation of the carbonium ion responsible for exchange. The following gas phase heats of reaction for the formation of the most likely carbonium ion from the parent molecules of ethylene, propylene, 1-butene, isobutene and isobutane have been evaluated from thermochemical data.⁽²¹⁴⁻²¹⁶⁾





In the evaluation of gas phase heats of reactions two values of $\Delta H_f \text{ OH}^-$ can be used. Field and Franklin⁽²¹⁶⁾ report a value of -39 Kcal/mole which is 37.4 Kcal/mole less endothermic than that used here.⁽²¹⁹⁾ Use of this other value however, will not affect the qualitative nature of the following discussion.

For the reactions of hydrocarbons on the zeolites it can be seen that the activity of the catalysts roughly parallel the ease of formation of the corresponding carbonium ions. Although, as is demonstrated for the case of propylene, it is easier to form radicals than ions on reaction with water in the gas phase, the polar nature of the zeolite surface is obviously sufficient to reverse the energy situation in the catalytic

reaction. The excess energy required to form ions over that for radicals, which amounts to ~ 80 Kcal/mole is probably compensated for by the high interaction energies of the ions with the zeolite surface. This interaction is higher for the multivalent ion exchanged sieves than for the monovalent ones.⁽¹⁷⁸⁾ The energy gain for monovalent ion exchanged zeolites may not be sufficient to compensate for the high heat of formation of the ions and so radical intermediates may be preferred on these sieves. This is in keeping with the experimental results which suggest that monovalent ion exchanged sieves promote reactions via radical mechanisms.⁽⁴⁷⁾

However ionic mechanisms are probably operative on multivalent metal ion exchanged sieves since the exchange of propylene is much faster than that for ethylene. If radical mechanisms were operative one would expect ethylene to be as reactive as propylene since as shown above the energies required to form alkyl radicals from both molecules are very similar. Although if radical intermediates were involved in exchange there may be slight differences in the rates of reactions due to other causes, the large differences in activity noticed in this work could not be explained on this basis. This is also borne out by the fact that on metal catalysts where adsorbed radicals are thought to be important this large difference in the reactivities of the two molecules is not observed.⁽²¹⁷⁾ Thus the exchange reactions of propylene

and ethylene can be used as tests for reaction mechanisms, where large differences in activities should be found if the reactions proceed via ionic mechanisms and only minor differences result if adsorbed radicals are the reaction intermediates.

In the case of the ion-exchanged zeolites used here NiX seems to be somewhat anomalous. For this catalyst the exchange of ethylene was only about 10 times slower than the reaction with propylene compared with factors greater than 1,000 for the other zeolites. The conclusion drawn from these facts is that the reaction on NiX may be of a partly radical nature whereas predominantly ionic intermediates occur on the CoX, CeX and LaX zeolites. The ability of NiX to catalyse the hydrogen-deuterium exchange reaction and readily hydrogenate ethylene at 0°C could also be due to this tendency to form adsorbed radicals rather than ions.

There is another point to note here in connection with results for the reactions of hydrocarbons with deuterium. As can be seen from the thermochemical data alkyl radicals are more easily formed and carbonium ions harder to obtain when reactions are carried out with deuterium gas instead of heavy water. Thus reactions with D₂O may tend to accentuate the carbonium ion character of catalysts whereas reactions with D₂ may tend to suppress them. This could help to explain the predominantly radical nature of the reaction of alkyl benzenes

with Deuterium on NiX reported by Pope and Kemball.⁽⁴⁸⁾

4.3. Nature of the active sites

Since the catalytic activity of the zeolite depends upon the cation present, the exchange of one cation for another must alter the active site. Figure 4.4. shows how the activity of the zeolites for the exchange of propylene vary with increasing amounts of exchange of the Na^+ ions for Ni^{++} and Ce^{+++} ions. In both cases replacement of about 20% of the available Na^+ ions by these other ions results in a large increase in activity, the exchange reaction taking place at temperatures over 100°C lower than with NaX. Further degrees of exchange of the Na^+ ions results in a less marked increase in activity. The results on NiX zeolites are somewhat similar to those found by Pope and Kemball⁽⁴⁸⁾ where the catalytic activity of these zeolites for the exchange of benzene with deuterium rose sharply after small amounts of replacement of Na^+ by Ni^{++} ions, although the trend was much more pronounced in their case.

These results however, are in marked contrast to others reported for the isomerisation of n-hexane on calcium exchanged X sieves.⁽¹⁶⁹⁾ Here exchange of the first 10% of the Na^+ ions for Ca^{++} ions did not give any appreciable increase in catalytic activity over that found for NaX. The 40% exchanged sieve had only a moderate activity while the 80% exchanged sieve was highly active. These results can be explained by assuming

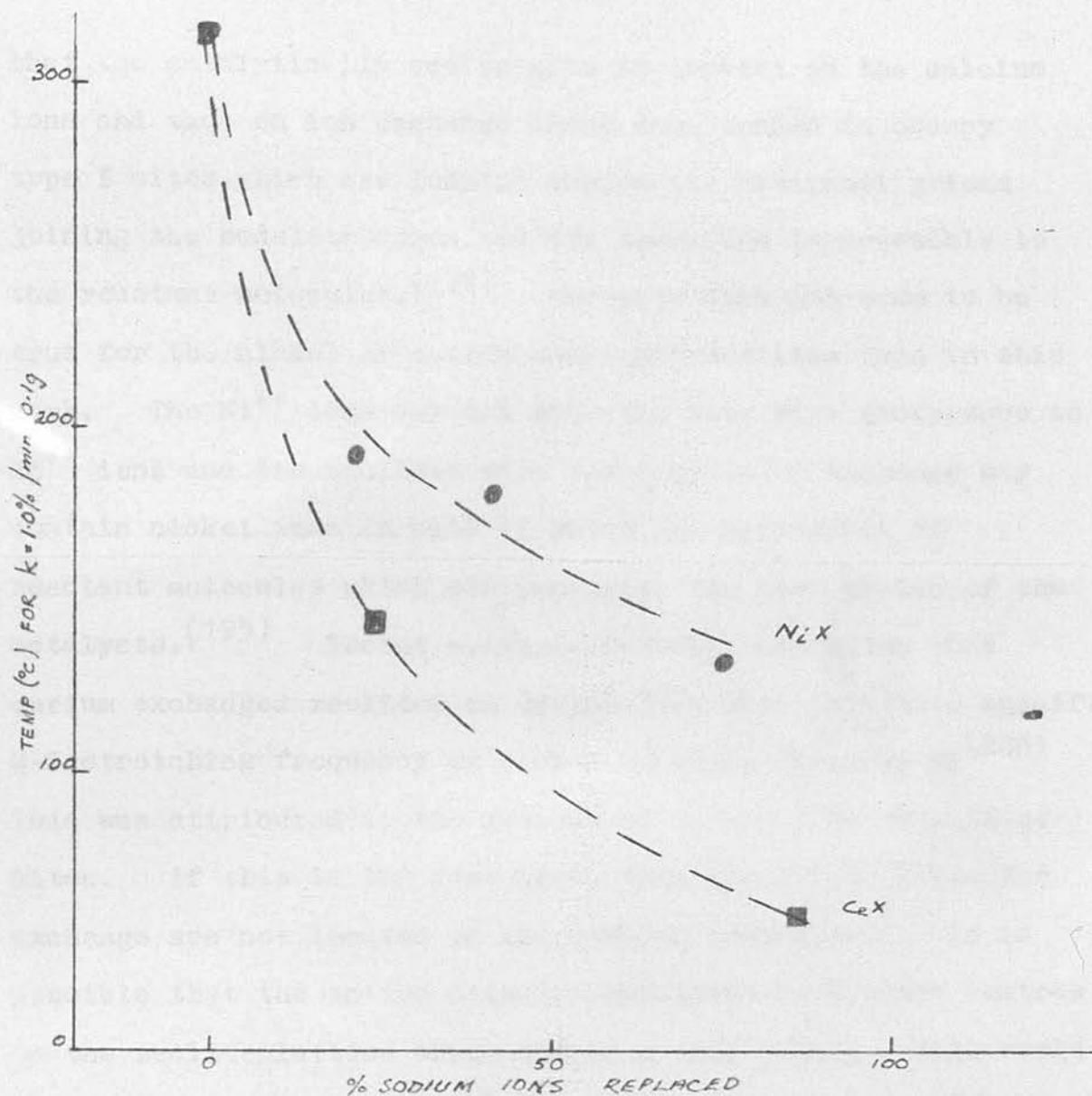


FIGURE 4.4

VARIATION IN CATALYTIC ACTIVITY FOR PROPYLENE/D₂O EXCHANGE
WITH DEGREE OF REPLACEMENT OF Na⁺ BY Ni⁺⁺ AND Ce⁺⁺⁺
IONS IN X TYPE ZEOLITES

that the catalytically active site is located on the calcium ions and that on ion exchange these ions tended to occupy type I sites which are located inside the hexagonal prisms joining the sodalite cages and are therefore inaccessible to the reactant molecules.⁽¹⁷⁵⁾ The same does not seem to be true for the nickel or cerium exchanged zeolites used in this work. The Ni^{++} ions may not show the same site preference as Ca^{++} ions and the zeolites with low degrees of exchange may contain nickel ions in site II which are accessible to reactant molecules which can penetrate the pore system of the catalysts.⁽¹⁹⁵⁾ Recent evidence however, has shown that cerium exchanged zeolites on dehydration show no cation specific C-O stretching frequency on carbon monoxide adsorption.⁽²⁰⁶⁾ This was attributed to the absence of cerium ions in surface sites. If this is the case here, then the active sites for exchange are not located on the cations themselves. It is possible that the active site is associated with other centres on the zeolite lattice which act as strong acids. This would explain the parallel found between the catalytic activity of the zeolites used here and the total acidities measured by others for similar zeolites.⁽¹⁸³⁾ The variation in activity shown by the different ion exchanged zeolites may simply be due to the effect of the cation on the number and strength of these acid sites.⁽¹⁹³⁾

The effect of the addition of increasing amounts of water

to NiX, CoX and CeX was to lower the activity of the catalyst and increase the activation energy of the reaction for the exchange of propylene. Thus water must be adsorbed on the active site for exchange and effectively shield it from the reactant molecules. These results are again contrary to many of those published in the literature where addition of water to the catalyst increased the activity for the isomerisation of cyclopropane over NaY,⁽²¹⁸⁾ for Friedel Crafts reactions on multivalent metal exchanged sieves,⁽⁴²⁾ and for the adsorption of CO₂ on NaX.⁽¹⁹⁴⁾ Nishizawa et al.⁽¹⁸³⁾ report that on the addition of water to X type sieves at 200°C Brönsted acid sites appeared especially on CaX, CeX and LaX but not on NiX. The catalytic activity for polymerisation of propylene was increased on CaX, ZnX and MnX by the addition of water but not in the case of MgX, BaX or LaX sieves, whereas in the work reported here adsorption of water had a poisoning effect on the polymerisation of propylene if present in large quantities although the polymerisation activity of CuX seems to be increased on the addition of one water molecule per cage. However, Topchieva et al.⁽¹⁸²⁾ report that for cumene cracking on divalent and trivalent forms of zeolite Y, water promoted the catalyst only if it was added at temperatures higher than 436°C, which they attributed to the strong chemisorption of water below these temperatures. In this connection it is perhaps noteworthy that in the experiments reported here the water was adsorbed on

the catalyst at room temperature and in no case was the temperature on reaction raised above 190°C.

The adsorption of water on divalent cation exchanged Y molecular sieves (MY) has been reported to take place on the metal ions giving MOH^+ and structural OH groups which are catalytically active.⁽¹⁹³⁾ A scheme is presented whereby the zeolite, through the interaction of the metal ions with adsorbed water molecules, is a source of H^+ ions. The cations with the higher electrostatic fields yield more H^+ ions and hence increase the catalytic activity. This is in contrast to the conclusions drawn by Rabo et al.⁽¹⁷⁰⁾ who report that the catalytic activities of the X and Y type sieves follow the changes in electrostatic fields and are independent of the presence of OH groups. However there is growing opinion^(193,219) that in many cases the simple concept of the cation polarising power is insufficient to explain the experimental results obtained, although there is little doubt that the majority of the multivalent metal exchanged zeolites catalyse reactions by their ability to form carbonium ions from reactant molecules.

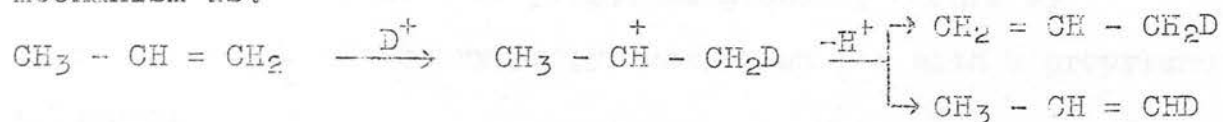
4.4. The Mechanisms of exchange of hydrocarbons

The following discussion shows how the carbonium ion theory of reaction mechanisms can be applied to explain the nature of the results obtained for the reactions of the various

hydrocarbons with D₂O on zeolites and the similarity between these results and other results published in the literature.

Propylene

The mechanism for the exchange of propylene must explain the result that only five of the six hydrogen atoms in the molecule are easily exchangeable and that these five all react at similar rates by a stepwise process. The most likely mechanism is:

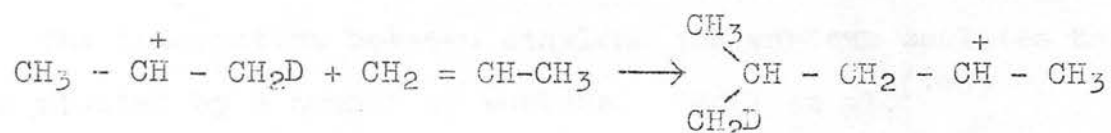


where a carbonium ion is formed by attack of a D⁺ on the propylene molecule. This means that on adsorption both terminal groups are made equivalent. On reversal to a propylene molecule, through loss of a proton, the propylene can appear with one deuterium atom in either of the terminal groups but the middle hydrogen in the molecule cannot be replaced.

A similar mechanism for the exchange of propylene has recently been proposed by Habgood et al.⁽²¹⁸⁾ for reaction on D₂O loaded NaY zeolite. This zeolite had an activity higher than that found in this work for NaX. Only five hydrogens were exchangeable and it was shown, by the inability of this catalyst to effect the exchange between CH₃ - CD = CH₂ and H₂O on the zeolite, that the middle hydrogen atom was the one which was unreactive. Hall et al.⁽¹⁹⁰⁾ also report the formation of

carbonium ions from the reaction of propylene with the CH groups of decaionated zeolites. Further evidence for this mechanism for exchange is found from I.R. work on the adsorption of olefins on Y type sieves⁽²²⁰⁾ where it was found that on adsorption most olefins lose their double bond character. This could be explained by the formation of the carbonium ion postulated above.

The polymerisation of propylene probably occurs by reaction of the secondary propyl carbonium ion with a propylene molecule:



The similar activities of the CeX and LaX zeolites for exchange and polymerisation suggest that the same sites and intermediates are involved in both processes. For divalent exchanged sieves the situation is more complex, CuX being more active for polymerisation than exchange and NiX having comparable activities for both processes while on CoX little polymerisation takes place at temperatures where the exchange reaction is rapid. In the reactions where polymerisation was occurring along with exchange it was found that the exchange reaction was a true first order process since the rate was independent of the absolute amount of reactant present.

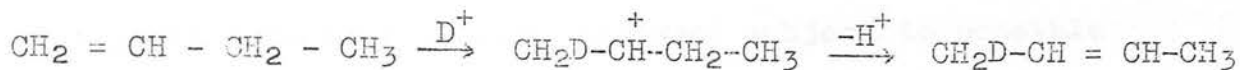
Ethylene

As discussed previously the decreased activity of the catalysts for the exchange of ethylene over that found for propylene is probably a consequence of the greater difficulty in forming a primary ethyl carbonium ion from the ethylene molecule. Such a carbonium ion intermediate would lead to the stepwise replacement of all four hydrogen atoms in the molecule. NiX seems to have an anomalously high activity for this reaction and in this case radical intermediates may be important.

The interaction between ethylene and various zeolites has been studied by a number of workers. Hall et al.⁽¹⁹⁰⁾ suggest that the adsorption of ethylene on decationated X and Y zeolites took place on the acidic OH groups of the zeolite which act as Brönsted acids to reasonably strong bases. However ethylene may also adsorb on cation exchanged zeolites in other ways. Carter et al.⁽²²¹⁾ demonstrated both spectroscopically and calorimetrically that ethylene formed complexes with the cations of zeolites and that the properties of these complexes depended critically on the cations present. Eberly⁽²²²⁾ has also shown that the degree of interaction between olefins and Y type zeolites increases with the electronegativity of the cation in the sieve.

1-Butene

The mechanism for the exchange of 1-butene must explain the greater ease of replacement of one hydrogen atom in the molecule. Such a scheme is discussed below:



As with propylene a carbonium ion is formed by attack of a D^+ on the terminal CH_2 group. Thermodynamic arguments show that when this carbonium ion loses a proton in reverting to gas phase butene it will tend to form 2-butene rather than 1-butene. This is easily seen from a consideration of the thermodynamic equilibria of the various butenes. At 20°C the equilibrium percentages of the butenes are 2.5%, 23.4% and 74.1% for 1-butene, cis-2-butene and trans-2-butene respectively and so the carbonium ion will tend to revert to the cis and trans isomers rather than 1-butene. Thus to obtain further replacement of hydrogen by deuterium in the molecule the D^+ has to act on 2-butene rather than 1-butene:



The large build up of the d_1 species in the observed distribution of products can be explained if attack at the secondary carbon atom of 2-butene is more difficult than attack on the primary carbon atom of 1-butene. Such a mechanism should however lead to a build up at the d_3 isotope also. The reason this was not found could be because at this extent of reaction

the butenes should be in equilibrium and the smaller amount of 1-butene in the gas phase, required to obtain further exchange of the terminal groups, was compensated for by its greater reactivity. The experimental product distributions at high extents of reaction, although subject to possible errors made in the assumption that the fragmentation patterns of all the butenes were similar, show that all eight hydrogen atoms in the molecule are exchangeable.

Evidence that attack on the secondary carbon atom of 2-butene is more difficult than attack on the primary carbon atom of 1-butene can be obtained from butene isomerisation data. Hightower, Gerberich and Hall⁽²²³⁾ report that on silica-alumina the order of reactivity of the three butenes is 1 butene \gg cis- \gg trans-2-butene. Since it was also suggested⁽²²⁴⁾ that the rate determining step in these reactions is proton transfer to form the 2-butyl carbonium ion intermediate the differences in activities of the three butenes must be attributed to the differences in the ease of formation of the carbonium ions. Ozaki and Kimura⁽²²⁵⁾ also concluded from their work on n-butene isomerisation over D₂O soaked acid type catalysts that the isomerisation proceeded through a protonic mechanism. Their results for the deuterium content of the butenes produced on reaction are similar to those reported here where a large excess of the D₁ compound was formed. Their results also show that initially this deuterium content is

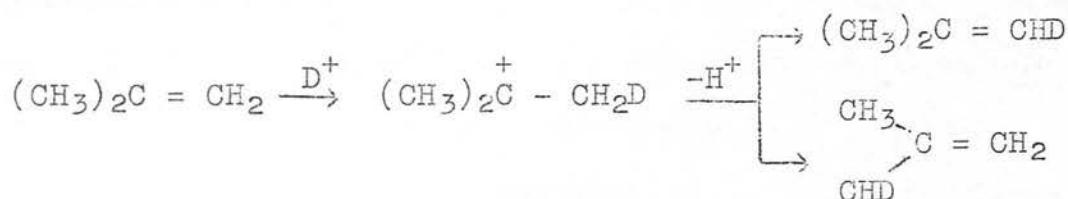
shared almost exclusively by the cis and trans isomers but that at greater extents of reaction more deuterium can enter into the 1-butene.

There is also some evidence that the reactivities of zeolites for isomerisation of butenes are similar to those reported for silica-alumina catalysts. On NiX zeolites the order of reactivity is 1 butene > cis- >> trans- 2-butene⁽¹⁹⁶⁾ and similar results have been found for CuX zeolites.⁽²²⁶⁾

The polymerisation of 1-butene on CeX probably occurs by a process similar to that for propylene.

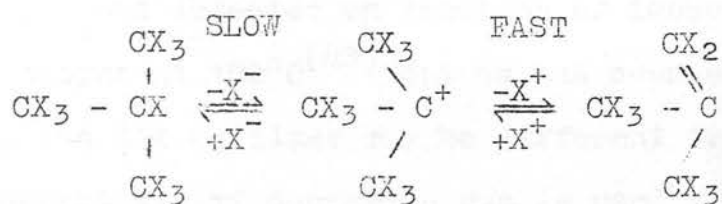
Isobutene and Isobutane

The extremely easy exchange of the hydrogen atoms in isobutene is a consequence of the ease of formation of the tertiary carbonium ion intermediate:



All eight hydrogen atoms are exchangeable by this process in a stepwise manner. In the exchange of isobutane the same tertiary carbonium ion intermediate is also probably formed, the increase in temperature required for reaction of isobutane over isobutene being due to the difficulty of formation of this ion from the former molecule. Once formed this carbonium ion can undergo several transitions between the ion and the

adsorbed olefin^{before} reverting to the gas phase as isobutane. The transitions between adsorbed carbonium ion and olefin, which are likely to occur many times before desorption in view of the much greater reactivity of isobutene, lead to the incorporation of many deuterium atoms into the isobutane ~~molecule~~ ^{molecule} per adsorption/desorption step thus giving the large amounts of the d₇ d₈ and d₉ isotopes found on reaction on CeX and LaX.



X = H or D

The reaction on CeX and LaX demonstrates the mobility of these adsorbed species since although the ratio of D₂O to hydrocarbon was only 2:1, equivalent to 4D atoms per 10 H atoms, each reacted isobutane molecule contained an average of 8 D atoms. The lower amounts of multiple exchange on CoX and NiX may be attributed to their poor activity and the high temperatures used to obtain noticeable reaction.

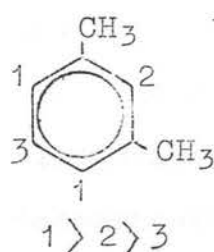
Similar exchange patterns have been found for the reaction of isobutane on silica-alumina and other catalysts.^(130,131) The absence of the d₁₀ isotope in the initial products was proposed to be due to the nature of the regeneration of isobutane from the tertiary carbonium ion which was suggested

to occur via hydride ion abstraction from another isobutane molecule. This could also explain the absence of the d_{10} isotope found in this work although on the other hand since maxima were found at the d_7 and d_8 isotopes with less d_9 there would be expected to be little d_{10} if the deuterium atoms were distributed randomly among all ten positions. The sensitivity of the apparatus and the accuracy of analysis may not have been sufficient to detect this small amount of the d_{10} isotope. On NiX the d_{10} isotope was detected on reaction of isobutane with D_2 on 1 gm. catalyst at $190^\circ C^{(48)}$ but as has been shown ~~PREVIOUSLY~~ previously, the NiX catalyst may be different from the other catalysts especially if deuterium gas is used as a reactant instead of D_2O .

m-Xylene

The reaction of m-xylene with D_2O on CoX and CeX zeolites show that the hydrogen atoms in this molecule can be classified in three groups according to their ease of exchange. The first group to undergo exchange contains three hydrogen atoms while the second and third groups contain one and six atoms respectively. Although from mass spectrometric data alone the position of these various hydrogen atoms in the molecule cannot be determined, it seems likely that the first two groups of atoms to exchange are those in the aromatic ring and the last group consists of the six hydrogen atoms on the two methyl side groups.

If the mechanism for exchange of m-xylene is similar to that for exchange of the other unsaturated hydrocarbons, namely attack of a D^+ at reactive positions in the molecule, then it would be expected that the ease of replacement of the various hydrogen atoms would parallel the ease of electrophilic attack at these positions. From this point of view the ring hydrogens should be most reactive and should separate into three groups according to reactivity as shown in the diagram, owing



to the electron donating effects of the methyl side groups. Such effects have been noticed in the homogeneous acid catalysed exchange of the alkylbenzenes^(55,134,135) and have been discussed in Part II Chapter 4 of this thesis. The results reported here are similar to those obtained in acid media with the exception that there were only two groups of different reactivity among the ring hydrogen atoms. The hydrogen atom in the second group could be attached to the carbon atom ortho to the two side groups but it is more likely to be the one in the meta position. Confirmation of this could be obtained from a study of the reactions of the other alkylbenzenes and mesitylenes.

The results reported here are of a similar nature to those reported for exchange of toluene on a partially deuterated hydrogen Y zeolite⁽¹⁴⁴⁾ and lie closer to those for homogeneous acid catalysis than do those reported earlier for the reaction of m-xylene with deuterium on silica-alumina and alumina.

Different results were obtained however, for the reaction of m-xylene with deuterium on NiX zeolite.⁽⁴⁸⁾ In this case the six side-group hydrogen atoms reacted in preference to those in the ring positions and the atoms in the ring positions all exchanged at similar rates. These latter results are more similar to those found in catalysis by metal than by acids and again ^mexphasise the anomalous behaviour of NiX, although as discussed previously the results may be different if D₂O is used as a source of deuterium.

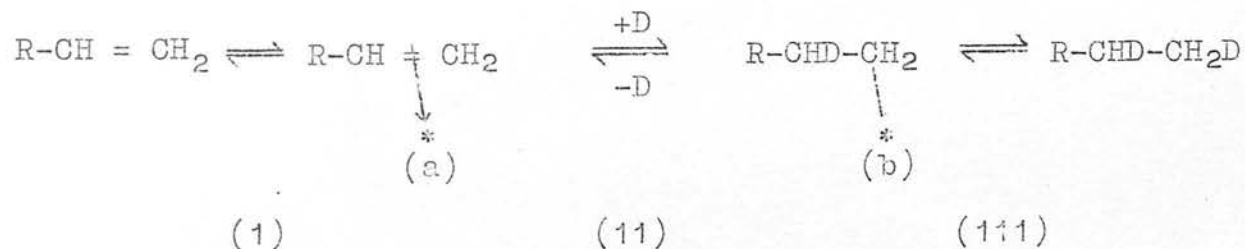
The presence of different reaction rates among the various ring hydrogen atoms demonstrates that at these temperatures isomerisation of m-xylene was unimportant compared with exchange. Comparisons of the temperatures required for exchange show that for CeX containing 11.1 molecules D₂O per cage the first three hydrogen atoms start to exchange at ~60°C, the fourth at ~140°C and the last six at ~200°C (130°C, 200°C and 260°C for CoX). Thus the first group of hydrogens are more reactive than those in propylene while the others although less reactive than propylene are more reactive than ethylene or isobutane.

4.5. Reactions with hydrocarbon - deuterium mixtures

On reaction of ethylene with deuterium on NiX hydrogenation was the predominant reaction and took place easily at 0°C giving ethane d₂ as the major product. The reaction of propylene was slower with both exchange and hydrogenation taking place.

Exchange of the paraffins formed from both olefins was negligible at temperatures where the other reactions were rapid.

The exchange and hydrogenation of ethylene and propylene have been the subject of much research and a review of this work has been published by Bond and Wells.⁽²²⁷⁾ The difference between much of the work carried out on the hydrogenation over metal catalysts and those for NiX lies in the fact that the major hydrogenation product is alkane d₂ on NiX whereas on other nickel catalysts many other isotopic ethanes are produced as initial products due to the various interactions of surface intermediates which take place. The interesting point about the work reported here is that although on most molecular sieves the exchange of ethylene is much slower than propylene yet on NiX the hydrogenation reaction is much faster. Adsorbed radicals rather than carbonium ions are probably the reactive intermediates. Possible mechanisms are given below.



Exchange of the olefins result from the interconversion of intermediates (a) and (b) with consequent desorption via step (1) while hydrogenation results from step (111). The relative

importance of the two reactions depends on the ease of the various steps.

4.6. Conclusion

The main conclusions to be drawn from the present work on zeolites can be summarised as follows. They are poor catalysts for H_2/D_2 exchange which may be due to their tendency to form adsorbed ions from reacting molecules rather than radicals or atoms. When contacted with D_2O they act as acid catalysts carrying out reactions of hydrocarbons via carbonium ion intermediates. NiX zeolite shows many anomalies and it is believed that in this case adsorbed radicals may be important. Other data give some clues as to the nature of the effect of hydrogen on the zeolite and the location of the active sites for exchange but more data will be required before any firm conclusions can be drawn.

Appendix

In January 1968 a report published by the Royal Society Conference of Editors, recommended that the metric system of units, known as SI, should be adopted in all scientific and technical journals. SI, which is the abbreviation in many languages for *Système International d'Unités*, is an extension and refinement of the traditional metric system. It embodies features which make it logically superior to any other system as well as practically more convenient. In these units the metre and the kilogramme take the place of the centimetre and gramme of the old metric system. The unit of force is the newton (kg m s^{-2}) and that of energy is the joule ($\text{kg m}^2\text{s}^{-2}$). Multiples and fractions of units are normally to be restricted to steps of a thousand and their symbols are given below.

FRACTION	PREFIX	SYMBOL	MULTIPLE	PREFIX	SYMBOL
10^{-3}	milli	m	10^3	kilo	k
10^{-6}	micro	μ	10^6	mega	M
10^{-9}	nano	n	10^9	giga	G
10^{-12}	pico	p	10^{12}	tera	T
10^{-15}	femto	f			
10^{-18}	atto	a			

Compound prefixes should not be used, e.g. 10^{-9} metre is represented by:

$$1 \text{ nm} \quad \text{not} \quad 1 \text{ m}\mu\text{m}$$

The attaching of a prefix to a unit in effect constitutes a new unit, e.g.

$$1 \text{ km}^2 = 1(\text{km})^2 = 10^6 \text{ m}^2$$

$$\text{not} \quad 1 \text{ k(m)}^2 = 10^3 \text{ m}^2$$

Where possible any numerical prefix should appear in the numerator of an expression. The following are some units which are relevant to the work in this thesis

Physical Quantity	Name of Unit	Symbol for Unit
Length	metre	m
mass *	kilogramme	kg
time †	second	s
electric current	ampere	A
thermodynamic temperature	degree Kelvin	°K
customary temperature, t	degree Celsius	°C
energy	joule	J
force	newton	N

* the gramme can also be used as an elementary unit until such time as a new name may be adopted for the kilogramme

† the common units of time (e.g. hour, year) can also be used.

Since the writing of this thesis had begun before the publication of this report from the Royal Society, many values in the text are quoted in non - metric units. A table for conversion of these units into SI units is given below. Fuller lists can be found in the National Physical Laboratory's "Changing to the Metric system"

(Anderson and Brigg). London: H.M.S.O. (1966)

Physical Quantity	Old Units	equivalent in SI units
length	angström	10^{-10} m
pressure	inch torr	0.0254 m 133.322 Nm^{-2}
energy (activation energy)	calorie (kilocalories/gramme molecule)	4.184 J (4.184 MJ/kg. mol.)
energy	electronvolt (eV)*	1.6021×10^{-19} J
volume	litre (l)*	$10^{-3} \text{ m}^3 = \text{dm}^3$

*can be used in conjunction with SI units

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Exchange Reactions of Benzene, Toluene, and *m*-Xylene with Deuterium on Silica-Alumina and Alumina Catalysts

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Exchange Reactions of Benzene, Toluene, and *m*-Xylene with Deuterium on Silica-Alumina and Alumina Catalysts

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The exchange reactions of benzene, toluene, and *m*-xylene with deuterium have been studied on two silica-alumina catalysts containing 13% (I) or 45% (II) alumina and on pure alumina. The temperature ranges studied were 125–440°, 20–100°, and 20–250° for the three catalysts respectively. On any catalyst the hydrogen atoms in the ring positions of all three hydrocarbons reacted at the same rate and there were no appreciable directing effects due to the side-groups. Rates of reaction were substantially lower on silica-alumina I than on the other catalysts. Side-group exchange with toluene or *m*-xylene was slower than ring exchange by factors ranging from 30 upwards. Subsidiary experiments on hydrogen-deuterium exchange and on the isomerization of *m*-xylene were also carried out. Silica-alumina I was the least active for hydrogen-deuterium exchange and isomerized *m*-xylene at rates comparable with those found for side-group exchange.

CATALYTIC exchange reactions of alkylbenzenes with deuterium have been studied on metal films,¹⁻³ supported platinum,⁴ chromium oxide gel,⁵ titania,⁶ and nickel-exchanged zeolites.⁷ These reactions provide a useful method of investigating catalysts because of the different types of carbon-hydrogen bond present in the alkylbenzenes and the results already reported show striking variation in the relative ability of the various catalysts to bring about the exchange of side-group and ring hydrogen atoms. The purpose of the present work was to investigate the activity of silica-alumina and alumina catalysts for the exchange of the hydrogen atoms in benzene, toluene, and *m*-xylene. We wanted to find out to what extent the behaviour of these oxides differed from the other classes of catalyst studied. A further

reason for choosing silica-alumina was to determine whether the effects which have been shown to apply in the homogeneous acid-catalysed exchange reactions of alkylbenzenes⁸ were also noticeable on a typical heterogeneous catalyst of the acidic type.

EXPERIMENTAL

Apparatus.—The main features have been described.⁹ The apparatus consisted of a gas handling system with a silica reaction vessel (volume 190 cm.³) linked by a fine capillary leak to a Metropolitan Vickers MS2 mass spectrometer. In this way frequent analyses of the gas from the reaction vessel could be made during each experiment.

Materials.—AnalaR samples of benzene and toluene were dried over Linde 5A molecular sieve and distilled under vacuum. *m*-Xylene was obtained as a 99.91% sample from the Chemical Standards Division of the N.P.L. All

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¹ E. Crawford and C. Kemball, *Trans. Faraday Soc.*, 1962, **58**, 2452.

² R. J. Harper and C. Kemball, 'Proceedings of the Third International Congress on Catalysis,' North-Holland, Amsterdam, 1965, vol. II, p. 1145.

³ R. J. Harper, S. Siegel, and C. Kemball, *J. Catalysis*, 1966, **6**, 72.

⁴ J. Hightower and C. Kemball, *J. Catalysis*, 1965, **4**, 363.

⁵ R. L. Burwell, jun., and C. J. Loner, ref. 2, p. 804.

⁶ I. J. S. Lake and C. Kemball, *Trans. Faraday Soc.*, 1967, **63**, 2535.

⁷ C. G. Pope and C. Kemball, to be published.

⁸ V. Gold, 'Friedel-Crafts and Related Reactions,' Interscience Publishers, New York, 1964, vol. II, p. 1253.

⁹ C. Kemball, *Proc. Roy. Soc.*, 1951, **A**, **207**, 539.

hydrocarbons were degassed before use by repeated cycles of freezing, pumping, and thawing. Deuterium (99.5%) was obtained from the Matheson Company and purified by diffusion through a palladium thimble followed by a liquid-nitrogen trap. Cylinder oxygen was dried by passage through a liquid-nitrogen trap.

Details of the catalysts are in Table 1. The two silica-alumina catalysts were commercial samples supplied by

TABLE 1
Nature of the catalysts

Catalyst	Surface area (m. ² /g.)	Alumina (%)	Impurities (%)	
			Na ₂ O	Fe
Silica-alumina I...	470	13	~0.02	~0.043
Silica-alumina II	118	45.1	~0.15	<0.1
γ -Alumina	370	100	<0.001	<0.002

the Agricultural Division of Imperial Chemical Industries Limited and the alumina sample (97% gibbsite, 3% bayerite) was obtained from Peter Spence and Sons, Ltd.*

Technique.—The procedure for activating the catalysts involved heating in oxygen (100 torr) for 3 hr. at 520°, followed by evacuation and a second oxygen treatment. Finally the catalyst was outgassed for 12 hr. at 520° at 10⁻⁶ torr. The whole procedure was repeated before each run. After cooling, a gas mixture of 2 torr of hydrocarbon and 40 torr of deuterium was admitted to the reaction vessel and the exchange reaction was followed at two or more temperatures. Mass-spectrometric analyses were carried out with an ionizing beam of 13v electrons for benzene and toluene and 17v electrons for *m*-xylene. The usual corrections were made to the observed peak heights of the ions to allow for naturally occurring heavy carbon and deuterium and for the fragmentation of the molecules.

The methods for determining the rate of exchange of the various types of hydrogen atom in the molecules have been described³ but the equations used will be summarized briefly. For a molecule in which all hydrogen atoms are replaced at the same rate the course of the exchange is given by equation (1) where k_0 is the initial rate of entry of deuterium atoms into 100 molecules of hydrocarbon and $\phi =$

$$\log_{10} (\phi_{\infty} - \phi) = -k_0 t / (2.303 \phi_{\infty}) + \log_{10} \phi_{\infty} \quad (1)$$

$\Sigma i d_i$, d_i being the percentage of isotopic species containing i deuterium atoms at time t , ϕ_{∞} is the equilibrium value of ϕ . The initial rate of disappearance of the light hydrocarbon k_0 can be obtained from equation (2). The ratio

$$\log_{10} d_0 = -k_0 t / 230.3 + \log_{10}(100) \quad (2)$$

k_0/k_0 gives the average number of deuterium atoms entering each molecule in the initial stages of the reaction. For molecules containing two groups of hydrogen atoms which react at different rates the plot according to equation (1) will not be linear although the initial and final portions will approximate to straight lines with different slopes. Under these circumstances modified equations³ similar in form to equation (1) have to be used to determine the rates of reaction.

RESULTS

Character of the Exchange Reactions.—The value of k_0/k_0 was unity for each system showing that stepwise exchange with the replacement of a single hydrogen atom at a time

was occurring with each hydrocarbon over the three catalysts. On each catalyst, the ring hydrogen atoms in toluene and *m*-xylene were exchanged more rapidly than the hydrogen atoms in the methyl groups. Evidence for this is given in Figure 1 which shows a curved plot for *m*-xylene according to equation (1) and linear plots on modified equations assuming that 4 atoms were replaced quickly and 6 more slowly.

Further evidence to confirm that the ring hydrogen atoms were replaced preferentially and that all ring positions were exchanging at similar rates was obtained from the distributions of products at various stages of the reactions. Some typical distributions for toluene are shown in Table 2 which illustrate the way in which products with up to

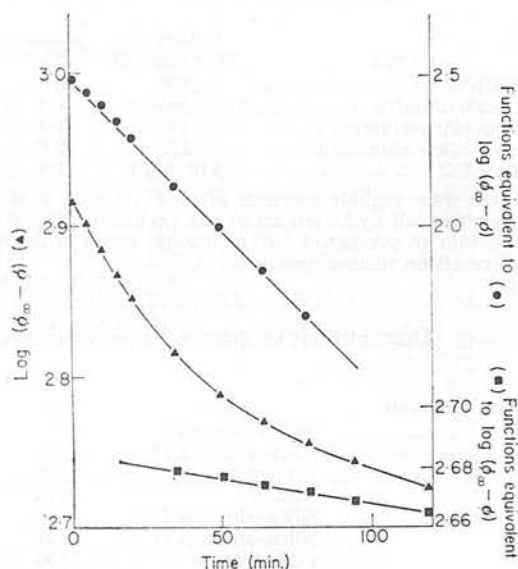


FIGURE 1 Rate plots for the exchange of *m*-xylene on silica-alumina I at 278°C: Δ , plot according to equation (1); \bullet , using a modified form of equation (1) assuming 4 exchangeable atoms; \blacksquare , the corresponding plot for the last 6 hydrogen atoms^{3,6}

5 deuterium atoms were formed in substantial quantity before large percentages of the molecules with 6, 7, or 8 deuterium atoms were produced. Comparisons may also be made with calculated distributions of products which are readily obtainable for the case of stepwise exchange.¹⁰ Under these circumstances, the percentage of the various isotopic hydrocarbons for a molecule in which all the hydrogen atoms are equally reactive can be derived at any stage of the reaction from the terms of the binomial expansion (3), where n is the number of exchangeable

$$100 \left(\frac{100n - \phi_t}{100n} + \frac{\phi_t}{100n} \right)^n \quad (3)$$

hydrogen atoms and ϕ_t is the value of ϕ at time t . For molecules with two groups of hydrogen atoms, a more complicated procedure must be used in which a binomial distribution is evaluated for each group by use of the appropriate value of ϕ in each case and then the two distributions are combined together. Two calculated distributions are given in Table 2; A corresponds to the

* See note added in proof on p. 1560.

¹⁰ C. Kemball, *Adv. Catalysis*, 1959, **11**, 223.

TABLE 2

Comparison of experimental and calculated product distributions for toluene exchange

Type	Extent of exchange (ϕ)	Product distribution (%)								
		d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
Calculated A ^a	412	0.5	3.7	12.2	23.1	27.3	20.6	9.7	2.6	0.3
Expt. on γ -alumina	416	0.2	0.5	3.0	16.6	40.3	38.4	1.0	—	—
Expt. on silica-alumina I	402	0.2	0.6	5.5	22.4	39.3	27.5	3.8	0.6	0.1
Expt. on silica-alumina II	402	0.1	0.5	4.4	21.0	41.7	31.3	0.9	0.1	—
Calculated B ^b	400 + 3	0.0	0.6	5.0	20.1	40.4	32.9	1.0	—	—

^a Distribution calculated for step-wise exchange assuming that all hydrogen atoms are exchanged at the same rate. ^b Distribution calculated on the assumption that the molecules contain an average of 4.00 deuterium atoms in the ring positions and 0.03 in the side group for comparison with experimental results on silica-alumina II.

TABLE 3

Comparison of experimental and calculated product distributions for *m*-xylene exchange

Type	Extent of exchange (ϕ)	Product distribution (%) ^a								
		d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
Calculated C ^b	280	3.7	14.6	25.5	26.4	18.0	8.4	2.7	0.6	0.1
Expt. on γ -alumina	280	1.4	9.2	25.1	37.6	25.2	1.4	0.1	—	—
Expt. on silica-alumina II	280	1.4	8.9	26.1	37.9	23.1	2.5	0.1	—	—
Expt. on silica-alumina I	271	2.0	12.3	28.3	33.2	18.8	4.6	0.7	0.1	—
Calculated D ^c	240 + 30	1.9	11.9	29.1	33.9	18.6	4.1	0.5	—	—

^a There were negligible amounts of products with 9 or 10 deuterium atoms. ^b Distribution calculated for step-wise exchange assuming that all hydrogen atoms are exchanged at the same rate. ^c Distribution calculated on the assumption that the molecules contain an average of 2.40 deuterium atoms in the ring positions and 0.30 in the side groups for comparison with the experimental result on silica-alumina I.

TABLE 4

Distributions to show the equivalence of the ring hydrogen atoms in the exchange reactions

Hydrocarbon	Catalyst	Extent of exchange (ϕ)	Product distribution (%)					
			d_0	d_1	d_2	d_3	d_4	d_5
Toluene	Silica-alumina I	261	2.4	13.5	30.2	32.3	17.5	4.1
	Silica-alumina II	262	2.3	13.1	30.4	32.7	17.5	4.0
	γ -Alumina	262	2.5	13.0	30.3	33.0	17.1	4.1
	Calc. E ^a	263	2.4	13.2	29.4	32.8	18.2	4.0
	Calc. F ^b	150	15.3	36.6	32.9	13.2	2.0	—
<i>m</i> -Xylene	Silica-alumina I	151	15.5	36.2	32.8	13.2	2.3	—
	Silica-alumina II	151	15.4	36.0	33.2	13.3	2.1	—
	γ -Alumina	150	15.2	37.2	32.1	13.4	2.1	—
	Calc. E ^a	151	15.4	36.0	33.2	13.3	2.1	—
	Calc. F ^b	150	15.3	36.6	32.9	13.2	2.0	—

^a Random distribution assuming 5 equally exchangeable hydrogen atoms. ^b Random distribution assuming 4 equally exchangeable hydrogen atoms.

distribution derived from equation (3) on the assumption that all eight atoms were equally reactive and as shown it differs markedly from the experimental distributions. On the other hand distribution B, based on two groups of atoms, is in excellent agreement with the result on silica-alumina II and equally good agreement was obtained with the experimental results on the other catalysts in a similar manner. Results for *m*-xylene are given in Table 3 and they confirm the evidence from the kinetic plots of Figure 1.

The distributions in Table 4 were obtained at earlier stages of reaction where side-group exchange was negligible. For each catalyst the experimental distributions corresponded closely to random distributions calculated on the assumption that only ring hydrogen atoms were replaced. This agreement shows that all the ring hydrogen atoms in each molecule are equally reactive in exchange.

Rates.—In order to compare the rates of exchange of the hydrocarbons a series of four runs was carried out using the same catalyst sample. Each series involved the exchange of benzene, toluene, *m*-xylene and finally benzene again with reactivation of the catalyst between each run. The results in Figure 2 for γ -alumina show the maximum decrease in activity between the initial and final runs with

benzene observed with any sample. With silica-alumina I the relative rates of the four runs were 1:0.5:0.4:0.8 and for silica-alumina II the ratios were 1:1.6:0.8:6.3.

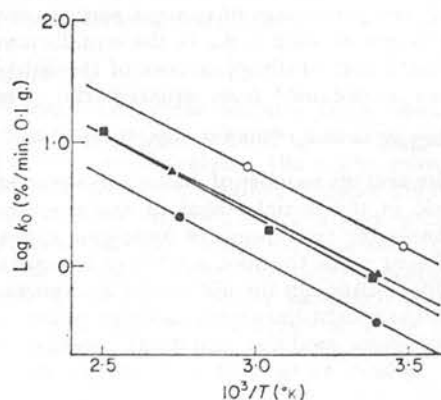


FIGURE 2 Arrhenius plots for a series of exchange runs on a sample of γ -alumina in the sequence benzene ○, toluene ■, *m*-xylene ▲ and benzene ●.

Repeat experiments with toluene and *m*-xylene on fresh samples of the two silica-alumina catalysts gave rates close

to those for the initial runs with benzene. A second series on a fresh sample of γ -alumina showed a maximum spread by a factor of 1.6 between any two runs with all the rates falling between those for the initial and final runs for benzene shown in Figure 2. These results showed that within the limits of reproducibility the ring hydrogen atoms in all three hydrocarbons were exchanging at the same rate on any one catalyst.

Because of the variation in catalytic activity from one run to the next we believed that it was preferable to derive Arrhenius parameters from rates obtained at two or three temperatures during the same run. In this way activation energies for ring exchange could be obtained with reasonable accuracy as is demonstrated by the parallel Arrhenius

dose of deuterium (18 torr) for 1 hr. followed by evacuation for 1 hr. at 520°. The normal rate of exchange was found after (b) and there was no evidence of any initial burst of reaction but after (a) the rate was slower by a factor of about 6 at 22°.

Isomerization of *m*-Xylene.—Some experiments were carried out to determine the rates of isomerization of *m*-xylene under similar conditions to those used for the exchange reaction. After reaction for a known time at a fixed temperature the hydrocarbon was frozen into a sample tube, diluted with pentane, and analysed by g.l.c. The column (12 ft.), which contained a packing (DE 210 LS 63547 from Perkin-Elmer) consisting of silicone oil MS 555, Bentone 34, and Chromosorb W in the ratios

TABLE 5
Rates and Arrhenius parameters for exchange

Catalyst	Exchange reaction	Temp. range (°C)	<i>E</i> (kcal./mole)	$\log_{10} A$ (<i>A</i> in molecules/sec. cm. ²)	Temp. for $k = 1\% / (\text{min. } 0.1 \text{ g.})^a$
Silica-alumina I ^b ...	Benzene	125–330	10.2 ± 1.0	14.2 ± 0.6	212°
	Toluene, ring	125–330	10.0 ± 1.0	13.6 ± 0.6	258
	Toluene, side group	300–440	13.8 ± 1.0	13.5 ± 0.6	547
	<i>m</i> -Xylene, ring	125–330	11.1 ± 1.0	14.3 ± 0.6	232
	<i>m</i> -Xylene, side group	300–440	13.4 ± 1.0	13.6 ± 0.6	441
Silica-alumina II ^c ...	Benzene	20–100	6.9 ± 1.0	15.7 ± 0.6	–5
	Toluene, ring	20–100	7.6 ± 1.0	15.9 ± 0.6	16
	Toluene, side group		0.06%/(min. 0.1 g.) at 100°		
	<i>m</i> -Xylene, ring	20–100	6.6 ± 1.0	15.8 ± 0.6	8
	<i>m</i> -Xylene, side group		0.6%/(min. 0.1 g.) at 100°		
γ -Alumina ^d	Benzene	20–130	6.0 ± 0.5	14.0 ± 0.3	27
	Toluene, ring	20–130	6.1 ± 0.5	14.1 ± 0.3	31
	Toluene, side group	150–250	12.3 ± 1.0	15.3 ± 0.6	205
	<i>m</i> -Xylene, ring	20–130	6.0 ± 0.5	14.0 ± 0.3	27
	<i>m</i> -Xylene, side group	150–250	11.9 ± 1.0	15.4 ± 0.6	172

^a Rates expressed as %/(min. 0.1 g.) are convenient for comparing catalyst activities. ^b The ratios of ring to side-group exchange for toluene and *m*-xylene at 300° were 81 and 29 respectively. The corresponding ratios at 100° were 280 and 70. ^c The corresponding ratios at 150° were 89 and 32.

TABLE 6
Isomerization of *m*-xylene

Catalyst	Reaction time (min.)	Reaction temp.	Composition of xylenes (%)			Initial rate [%/(min. 0.1 g.)]
			<i>o</i>	<i>m</i>	<i>p</i>	
Silica-alumina I	64	202°	—	100	—	—
Silica-alumina I	33	310	2	96	2	0.03
Silica-alumina I	33	390	11	77	12	0.23
Silica-alumina I	33	435 ^a	13	73	14	0.29
Silica-alumina II	30	98	—	100	—	—
γ -Alumina	30	236	—	100	—	—
Calc. for equilibrium		427	24.4	52.1	23.5	—

^a Some mesitylene detected.

plots found in different runs shown in Figure 2. Measurements on the exchange of the side-groups were less accurate because there was a tendency for the catalysts to become poisoned at the higher temperatures used. This poisoning was most noticeable on silica-alumina II and consequently reliable activation energies for side-group exchange could not be obtained. The rates and the Arrhenius parameters are summarized in Table 5. No loss of hydrocarbon from the gas phase was detected even when poisoning was occurring.

Specially treated γ -Alumina.—The exchange of toluene was followed on γ -alumina which had been subjected to two different pre-treatments: (a) after normal pre-treatment, exposure to oxygen (100 torr) for 30 min. at 520°, cooling to 20°, and evacuating for 1 hr., (b) after normal pre-treatment, exposure to deuterium (45 torr) for 1 hr. at 520°, and after evacuation for 10 min., exposure to a further

11.5:11.5:77, was operated at 100° with nitrogen as carrier gas (30 ml./min.) and a flame ionization detector. Typical retention times for *p*-, *m*- and *o*-xylene were 24.5, 28, and 30.5 min. respectively. Results are in Table 6. No isomerization occurred on γ -alumina or on silica-alumina II at temperatures which gave rapid ring exchange. On silica-alumina I isomerization of *m*-xylene was about 1/30th of the rate of ring exchange at 400° but the rates were similar to those for side-group exchange. Also the activation energy for isomerization was about 13 kcal./mole which is close to the value for the slower exchange process.

Hydrogen-Deuterium Exchange.—Reactions were carried out with equal pressures (13 torr) of hydrogen and deuterium. Rapid exchange occurred at –93° on both silica-alumina II and γ -alumina, the latter showing a slow reaction [0.05%/(min. 0.1 g.)] even at liquid-nitrogen temperature. In contrast, higher temperatures were

required for silica-alumina I (activated at 450°) which gave rates of 0.6 and 2.8%/(min. 0.1 g.) respectively at 153° and 199°. These values correspond to an activation energy of 13 kcal./mole and a frequency factor expressed as $\log_{10} A$ (A in molecule/sec. cm.²) of 17.1.

DISCUSSION

Variation in Activity.—The variations in activity are probably associated with minor differences in the pre-treatment of the catalysts which may include some variation in the amount of water retained on the surface. Hindin and Weller¹¹ have shown that both activation temperature and water content influence the activity of γ -alumina for the exchange of hydrogen and deuterium and for the hydrogenation of ethylene. Small traces of poisons may also contribute to the variation in activity. Larson and Hall¹² have shown that carbon dioxide poisons the exchange of methane and deuterium on γ -alumina.

Comparison with Homogeneous Acid Catalysis.—The common feature between our results and those for the homogeneous acid-catalysed exchange of the alkylbenzenes⁸ is that the ring hydrogen atoms react in preference to side-group atoms. However there are a number of differences between the two systems. On these oxide catalysts the side groups in toluene and *m*-xylene neither enhance the rate of exchange of the ring atoms nor cause directing effects favouring reaction at the *ortho* or *para* positions. Further, side-group exchange does occur, although slowly, on these oxides but it is found only in exceptional cases in homogeneous acid catalysis, e.g., with aromatic molecules containing the *t*-butyl side group.¹³ The absence of any appreciable isomerization of *m*-xylene at the temperatures used for ring exchange is important in relation to the equal reactivity of all four ring positions. If isomerization had been rapid compared with exchange, it would not have been possible to detect differences in the rate of reaction for the various ring positions.

Comparison with Metals or Other Oxides.—The exchange behaviour of the alkylbenzenes over silica-alumina and alumina is strikingly different from the results found with metals and some other oxide catalysts. With metals the side-group hydrogen atoms tend to exchange as fast as, if not faster than, ring atoms and there is usually some evidence of multiple exchange. On rutile⁶ all the hydrogen atoms in toluene exchange at similar rates whereas chromium oxide gel⁵ gives results similar to alumina, exchanging the ring atoms about ten times faster than those in the methyl group at 110°. All three oxides give predominantly stepwise exchange. The exchange of *m*-xylene with deuterium has now been studied on a number of catalysts and the results in Table 7 show the large range found for the ratio of ring to side group exchange. In general,

low ratios are found with catalysts such as the metals upon which adsorbed radicals are formed and large ratios are obtained with those oxides which would be more likely to give charged or highly polarised intermediates. The results indicate that the exchange of

TABLE 7

Exchange of *m*-xylene with deuterium on catalysts

Catalyst	Temp.	R *	Ref.
Pd film	0°	10 ⁻⁴	14
Sintered Ni film	20	10 ⁻²	1
Ni-X zeolite	170	10 ⁻¹	7
Fe, Pt, or W films	0	~1	14
TiO ₂ (rutile)	400	3	6
γ -Alumina	150	32	This work
Silica-alumina II	100	70	This work

* Ratio of ring to side-groups exchange.

m-xylene with deuterium may be a useful reaction for testing catalysts and for indicating the type of reactions which are likely to occur with hydrocarbon molecules.

γ -Alumina.—The main facts which emerge from our work and previous work with this catalyst are as follows: (a) The exchange between hydrogen and deuterium^{11,12} takes place readily at low temperatures and consequently there is no difficulty about 'activating' the hydrogen molecules for this particular exchange. (b) The rate of exchange of CD₄ with hydrogen¹² is close to the common rate that we find for the exchange of the ring hydrogen atoms in the three aromatic molecules. The rate of the methane reaction at 20° is 5.4×10^9 molecule/sec. cm.² compared with 3.7×10^9 in the same units for benzene exchange. The activation energy for both reactions are also similar (5.7 and 6.0 kcal./mole for methane and benzene respectively). (c) The surface hydroxyl groups on the catalyst exchange with deuterium much more slowly than the rate of the hydrogen-deuterium reaction. Temperatures of 50–100° or even higher are needed to bring about the replacement of the hydrogen associated with the surface.^{11,15,16} An approximate activation energy of 6 kcal./mole has been derived for the process¹⁵ but evidence based on spectroscopic studies showed that there is a range of rates for the replacement of different types of hydroxyl groups.¹⁶ (d) When CD₄ is used as the source of deuterium atoms only a fraction of the surface hydroxyl groups exchange rapidly at 135° which is a much higher temperature than that required for the exchange of methane with deuterium or for the equilibration of CH₄ and CD₄.¹² The sites which exchange readily at 135° number 7×10^{12} /cm.².

Larson and Hall¹² suggested that the cleavage of a carbon-hydrogen bond in methane was the slow step in the exchange reactions of methane. If a corresponding process which would probably be the formation of a new carbon-hydrogen bond for the exchange of ring atoms was rate-determining in our reactions it must be

¹¹ S. G. Hindin and S. W. Weller, *Adv. Catalysis*, 1957, **9**, 70.¹² J. G. Larson and W. Keith Hall, *J. Phys. Chem.*, 1965, **69**, 3080.¹³ G. Dallinga and G. Ter Maten, *Rec. Trav. chim.*, 1960, **79**, 737.¹⁴ R. J. Harper and C. Kemball, to be published.¹⁵ W. Keith Hall, H. P. Leftin, F. J. Cheselske, and D. E. O'Reilly, *J. Catalysis*, 1963, **2**, 506.¹⁶ J. L. Carter, P. J. Lucchesi, P. Corneil, D. J. C. Yates, and J. H. Sinfelt, *J. Phys. Chem.*, 1965, **69**, 3070.

chance that both methane and the alkylaromatic compounds exchange with deuterium at much the same rate. We believe that another possibility might be considered. The exchange of a hydrocarbon may only take place readily with deuterium atoms which are present in the form of OD groups at special sites and the rate-determining step might be the conversion of OH into OD at these sites. This suggestion would explain the equality between the rates of exchange of the ring atoms in the three aromatic molecules and the atoms in methane, the absence of directing effects due to the side groups in the aromatic molecules, the absence of any multiple exchange, and the fact that the activation energies of the exchange reactions are close to the approximate value for the replacement of surface hydroxyl by deuterium.¹⁵ However for this hypothesis to be tenable it is necessary to assume that a relatively small number of these special sites exist in order to account for the absence of an initial burst of reaction with toluene exchange on a catalyst pre-treated with deuterium at 520°. On the other hand, an assumption of less than 3×10^{12} sites/cm.² would be difficult to reconcile with the data from the poisoning experiments carried out by Larson and Hall.¹² Alternatively the absence of directing effects in the exchange of toluene and *m*-xylene could be explained if the reaction proceeded by a mechanism whereby the aromatic ring is bound to the surface by donation of π electrons to electron acceptor centres before exchange with deuterium. This sort of mechanism may not show preference for exchange in the *ortho* and *para* ring positions. The effect of the field gradients near the catalyst surface could also play an important role in the nature of the exchange reaction.

The slow step in the exchange of the side groups must be associated with the activation of the hydrocarbon and the exchange is likely to occur by a dissociative mechanism possibly involving a heterolytic cleavage of a carbon-hydrogen bond. Results with a wider range of alkylbenzenes including ethylbenzene and cumene would be useful in determining the mechanism of these reactions.

Silica-Alumina I.—The most noteworthy point is that this catalyst is much less active than γ -alumina for the exchange reactions of hydrogen and of the alkylbenzenes with deuterium. In this respect our results are in accord with others for silica-aluminas containing 10–13% alumina which show poor activity for exchange reactions of methane¹² and low rates of replacement of surface hydrogen by deuterium.¹⁵ Thus it appears that

the strongly acidic sites present on such silica-aluminas are not essential for the exchange processes we have investigated. With silica-alumina I the exchange of hydrogen with deuterium is only slightly more rapid than the reaction of the ring atoms of the alkylbenzenes but the latter exchange much more rapidly than methane in contrast to the results with γ -alumina.

Much of the previous work on exchange^{17–21} reactions using silica-alumina has involved pre-treating the catalyst with (or adding) D₂O and so the results cannot be compared directly with our measurements. The use of such pre-treated catalysts gives substantial amounts of multiple exchange and there is usually a maximum in the curve relating rate to content of deuterium oxide which acts as a poison if present in appreciable quantity. The order of activity of different molecules is olefins > saturated hydrocarbon containing tertiary carbon atoms \approx benzene > hydrogen > saturated hydrocarbons without tertiary carbon atoms.¹⁸ These results indicate that the ease with which the hydrocarbon can form carbonium ions is an important factor in exchange and also that there is a type of surface deuterium readily formed from D₂O which reacts more rapidly with some hydrocarbons, including benzene, than with hydrogen. The latter point supports the idea that a rate-determining step in our experiments on silica-alumina I, as on γ -alumina, might be the conversion of OH into OD at suitable sites.

It is noteworthy that side-group exchange and the isomerization of *m*-xylene have comparable rates and activation energies and hence possibly a common mechanism operates.

Silica-Alumina II.—This catalyst behaved more like γ -alumina than like silica-alumina I in every respect and it is probable that a separate alumina phase is present. The activation energies for the exchange of the ring atoms are similar on both silica-alumina II and γ -alumina and the higher activity of the former may be associated with a greater number of catalytic sites.

Note added in proof: A more detailed description of the gibbsite sample has been reported by Flockhart *et al.*²² Various forms of alumina^{23,24} can result from the dehydration of gibbsite depending on the size of the crystals, and it is possible that the conditions used in the present work lead to χ - and not to γ -alumina.

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